

CORRELATION EFFECTS AND ELECTRON DENSITIES  
IN SOME TWO-ELECTRON SYSTEMS

by

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### ABSTRACT

The first section of this work consists of an analysis of three wave-functions for the ground state of the two-electron series which begins with  $H^-$ . Two of the wave-functions include electron correlation. One does so by means of superposition of configurations and the other by the inclusion of explicit correlation factors. For comparison, the third function is of the Hartree-Fock type. The correlation within the wave-functions is demonstrated by presenting various density functions and density difference maps relative to the uncorrelated approach. Expectation values and physical properties such as X-ray scattering factors, diamagnetic susceptibilities and nuclear diamagnetic shielding factors are also presented. By this means it is possible to assess the correlation predicted by the wave-functions, with comparison being made where possible with results from a more accurate wave-function. In addition, the production of the natural expansion for one of the correlated functions gives extra information about the effects of radial and angular correlation. The second part consists of a study of a good one-centre treatment of the diatomic molecular ion  $HeH^+$ . Both the molecular formation and the electron correlation in the system are studied by means of density differences and expectation values. Natural orbitals are used to enable comparison to be made with another  $HeH^+$  wave-function. This comparison shows that the two calculations are similar, even though conceived quite differently. A development of the general theory of natural spin orbitals is given as an appendix. Special emphasis is given to this technique as regards two-electron systems.

GENERAL INTRODUCTION.

Since the very beginnings of quantum mechanics, two-electron systems have occupied a position of the highest importance and have been the objects of a great deal of interest. The reason for this is that they form a stepping-stone between the comparatively simple one-electron systems and the far more complicated systems with many electrons. The value of the pioneering work of Hylleraas in this field can hardly be overestimated. Since his original series of classic papers, the pace of the work on two-electron systems has never slackened. In fact, since the nineteen-fifties it has quickened considerably, with the advent of high speed electronic digital computers. During this modern phase the work of Pekeris has been especially noteworthy.

This present work is divided into two main sections. Part I is a study of the electron correlation in various theoretical treatments of an isoelectronic series. These approaches study the ground states of eight members of the two-electron series beginning with  $H^-$ . Part II is concerned with a calculation on the simplest heteronuclear diatomic system, the molecular ion  $HeH^+$ . In addition, an appendix contains a description of the theory of natural spin orbitals. This technique is used extensively during the work of Part I and Part II.

In Part I a close study is made of two treatments which

introduce correlation by different methods. These are two of the three methods which Hylleraas introduced in 1928. One method is by the superposition of configurations, of which the wave-functions of Weiss are examples. The other is by using explicit correlation terms in the wave-function, as was used by Green et al. General details of these two methods and a description of the actual treatments in which they were used are given in Chapter 2.

Examination of the correlation within each treatment is carried out by evaluating various density functions and expectation values for the correlated wave-functions and for the corresponding Hartree-Fock functions. These Hartree-Fock functions are due to Curl and Coulson and to Roothaan, Sachs and Weiss. Analysis of the configuration interaction functions in terms of natural spin orbitals enables a classification to be made in terms of radial and angular correlation. All this is presented in Chapter 3, whilst the discussion of the results is given in Chapter 4. Where possible, results are compared with corresponding values obtained from very elaborate correlated wave-functions - those of Pekeris and of Frankowski and Pekeris. Special consideration is given to the systems with atomic number  $Z = 1-3$ , whilst for  $Z = 4-8$  the analysis is less extensive and interest is concerned more with an examination for overall trends and general behaviour.

The molecule-ion  $\text{HeH}^+$  has received a good deal of attention

since the early days of quantum mechanics, and a very great variety of calculations has been performed on it. Part II of this work is devoted to an examination of a good one-centre wave-function for the system. This is the calculation of Stuart and Matsen. Chapter 2 contains the details of the treatment, which is then analysed from two viewpoints. In Chapter 3 the molecular formation is examined by looking at the whole molecule as the bond length changes. A number of density difference maps are drawn to show the changes which occur as the internuclear separation is varied. Then, in Chapter 4, the effects of electron correlation in the system are discussed, again using density differences. A natural spin orbital analysis is performed and the results are compared with those of a similar analysis on a different wave-function for  $\text{HeH}^+$ . This wave-function is due to Anex and the NSO analysis was due to Anex and Shull.

Natural spin orbitals have an important place in this work, and for this reason an appendix is devoted to the general theory of NSO's for configuration interaction wave-functions. It is shown that by means of the natural expansion a simplification of a complicated configuration interaction wave-function may be achieved. This simplification is shown to be particularly striking in the case of two-electron systems. In this case also, a pleasing degree of physical interpretation of the wave-function is shown to be possible.

Tables of results, figures and references may be found at the end of the section to which they pertain.

**PART I**

CHAPTER 1.

INTRODUCTION.

The helium atom and the helium-like ions have been the subjects of a great deal of study throughout the history of quantum mechanics. Although exact analytical calculations on them are not possible, they are simple enough to allow extremely accurate approximate methods to be used. For the ground state, in particular, these approximate theoretical methods have reached the same degree of accuracy as that of spectroscopic measurements. In this respect therefore, such systems provide the ideal subjects for testing approximations which might later be extended to more complex systems.

The series of helium-like ions  $H^-$ , He,  $Li^+$ ,  $Be^{2+}$ , .....,  $O^{6+}$  are of considerable interest in physics and astrophysics. In particular, the existence of the negative hydrogen ion  $H^-$  has brought about an explanation of the opaque atmosphere of the sun <sup>(1)</sup>. This effect is caused mainly through the small concentration of hydride ions in the region immediately below the photosphere. Because of repetitive electron capture by neutral hydrogen and subsequent photodissociation through absorption of radiation from the sun's interior, the photosphere forms an optical boundary and gives the sun a sharp edge.

These systems are also particularly important, however, in any discussion of the correlation problem. As is explained later in this section, the essential consideration is of electrons with anti-parallel spins, which is precisely the situation which pertains in the ground states of the helium-like ions. The case of  $H^-$  provides a critical test of any approximation since it is only just stable against dissociation into a neutral hydrogen atom and a free electron. Because of this low binding energy, high accuracy is required of an approximation if it is to predict a bound state in this case.

Thus, in an analysis of electron correlation, such as this present work, some excellent material is provided by approximate wave-functions for the helium-like ions  $H^-$ , He, ..... $O^{6+}$ . We begin by giving a brief résumé of the problem of electron correlation and of various attempts which have been made to solve it.

#### The Correlation Problem:

In order to obtain accurate solutions of the Schrödinger equation for atomic and molecular systems, it is essential to take account of the so-called "correlation energy", which arises from the tendency of the electrons to avoid one another. This appears in the Hamiltonian as the Coulomb term  $\frac{1}{r_{12}}$ , and it is this term which causes great difficulty in the theory.

The approximation developed by HARTREE<sup>(2)</sup> and FOCK<sup>(3)</sup> has enjoyed great success in giving approximations to the wave-functions for electronic systems. However, this famous method suffers from one serious inadequacy; this is its inherent inability to account fully for the correlation of the electrons. The solution itself is based on the "independent particle" model. It is expressed as an antisymmetrized product of "one-electron functions", and implicit in this is the fact that electrons of like spin are surrounded by the "Fermi-hole" - that they are unlikely to be found close to one another. It is unable, however, to allow for the "Coulomb-hole" - that is, the tendency of electrons of unlike spin to avoid one another. It is in the light of this basic limitation of an otherwise excellent approximation that correlation energy has been defined<sup>(4)</sup> as the difference between the exact nonrelativistic energy and the energy from the Hartree-Fock method, i.e.

$$E_{\text{corr}} = E_{\text{nonrel}} - E_{\text{H-F}} \quad 1(1)$$

With this definition in mind, this analysis of certain correlated wave-functions has been undertaken. A solution of the Hartree-Fock type has been used as a standard "non-correlated" treatment, relative to which the merits of certain correlated treatments have been examined.

In his original study of the ground state of helium and of the He-like ions, HYLLEAAS<sup>(5)</sup> introduced three quantum-mechanical methods of treating electron correlation. These have been used continuously ever since, and have proved to be of the deepest importance in the development of this field.

Before describing these methods in detail, it is worthwhile mentioning at this stage a characteristic feature of the wave-function for two-electron systems. Describing only the singlet state (a similar procedure is possible for the triplet), the total antisymmetric wave-function may be factorized into a space part and a spin part:

$${}^1\Psi(\bar{x}_1, \bar{x}_2) = \Psi(\bar{r}_1, \bar{r}_2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad 1(2)$$

Here,  $\bar{x}_1, \bar{x}_2$  represent co-ordinates of space and spin, while  $\bar{r}_1, \bar{r}_2$  represent space co-ordinates only.  $\alpha$  denotes a spin component  $+\frac{1}{2}$  and  $\beta$  denotes a spin component  $-\frac{1}{2}$ . Thus,  ${}^1\Psi$  represents a total (antisymmetric) space-and-spin singlet wave-function, which may be factorized into the product of a symmetric space part and an antisymmetric spin part. In the case of the triplet, the space part is antisymmetric and the spin part symmetric. Because of this simplification for N (number of electrons) = 2, the main interest may be concentrated on the space functions.

The three methods introduced by Hylleraas have come to be commonly known by the following names:

- (a) Superposition of configurations.
- (b) Explicitly correlated wave-functions.
- (c) Different orbitals for different spins.

In the first method, also known as configuration interaction (CI), one chooses in theory a complete set of one-electron basis functions  $\psi_k(\bar{r}_i)$ . These are then combined to form the total wave-function, which may be written as

$$\Psi(1,2) = \sum_{kl} C_{kl} \psi_k(\bar{r}_1) \psi_l(\bar{r}_2) \quad 1(3)$$

with  $C_{kl} = C_{lk}$ . These coefficients are found using the variation method. In practice, the basis set cannot be complete because it would be unmanageable, and only a finite number of basis functions are chosen. Hylleraas found that the series of configurations converged rather slowly, and that far quicker convergence could be obtained by introducing the inter-electronic distance  $r_{12}$  explicitly into the solution. This method produced "explicitly correlated wave-functions", (b) above. Another application of this method was by JAMES and COOLIDGE<sup>(6)</sup> in their treatment of the hydrogen molecule. Method (c) is now described as the splitting of the closed shell,  $(1s)^2$ , into an open shell,  $(1s'1s'')$ , i.e. using different orbitals for

different spins (DODS).

Against the disadvantage of their slow convergence, configuration interaction wave-functions have the advantage that they may be generalized to systems with  $N$  greater than 2 without great difficulty. However, no physical significance can be placed on the configurations making up the total wave-function. To overcome this disadvantage, the original CI wave-function may be thrown into the form of the natural expansion, which is the superposition of configurations of most rapid convergence within a given basis. Details of the general theory of natural spin-orbitals are given in the Appendix.

Wave-functions containing  $r_{12}$  explicitly have enjoyed very great success, but certain drawbacks limit their application. Firstly, it seems impossible to give them a simple physical interpretation, and secondly, extension to include cases with more than two electrons produces extreme computational difficulties.

In the following pages, an analysis is presented of wave-functions which attempt to overcome the problem of electron correlation as outlined above. So great was the accuracy of the work of PEKERIS <sup>(7)</sup> that the "exact" correlation energy has been defined in terms of the difference between his energies and those from a Hartree-Fock treatment (c.f. equ. 1(1)).

CHAPTER 2.

WAVE-FUNCTIONS AND ENERGIES.

Wave-functions:

The wave-functions studied in this analysis of electron correlation are examples of two of the types of correlation, (a) and (b), discussed in the previous chapter. Thus the first type is a case of superposition of configurations, and the second arises from the inclusion of inter-electron co-ordinates explicitly. For each treatment of the ground state, the total wave-function was factorized to give a product of space and spin. The anti-symmetric spin function was then integrated out. Details of the individual treatments studied are given below, together with a description of the wave-functions which were used as criteria when comparing results.

Function I: This was the extensive CI calculation of WEISS <sup>( 8 )</sup>. In undertaking this calculation, his purpose was to investigate the method to see just how good were the results obtainable using expansions tractable on the existing computing equipment. At the same time, he sought a compromise between the accuracy of the approximation and its usability. His resulting normalized wave-functions for the two-electron series from  $H^-(Z=1)$  up to  $O^{6+}(Z=8)$  were superpositions of thirty-five

configurations. These were all the possible configurations which could be made up from the basis functions, which were: 1s, 2s, 1s', 2s', 3s'; 2p, 3p, 2p', 3p'; 3d, 4d, 5d; 4f, 5f; 5g. (Here, the prime among a group of orbitals with the same l quantum-number indicates a different orbital exponent.) This led to fifteen (ss) configurations, ten (pp), six (dd), three (ff) and one (gg). These basis functions were normalized Slater-type <sup>(9)</sup> orbitals (STO's), defined by

$$\psi_{n l m} = \frac{(2\eta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\eta r} Y_{l m}(\theta, \phi)$$

where  $r, \theta, \phi$  are spherical polar co-ordinates and  $Y_{l m}$  are spherical harmonics. Seven orbital exponents were used, obtained by optimization at a few selected points along the series, with graphical interpolation in between. This entire process was repeated for a 20-configuration function, but only the best function is studied here.

Function II: The functions of GREEN ET AL <sup>(10)</sup> were chosen as examples of accurate wave-functions which include correlation by means of explicit, Hylleraas-type terms. The total wave-function was of the form

$$\Psi(1,2) = f(r_1) f(r_2) g(r_1, r_2, r_{12})$$

and various analytical forms were chosen for the functions  $f(r_1)$  and  $g(r_1, r_2, r_{12})$ . The energetically "best" functions were, for  $Z = 1 - 5$ :

$$f(r_1) = \exp(-Zr_1) + c.\exp(-kZr_1)$$

$$g(r_1, r_2, r_{12}) = 1 + \alpha r_{12} + \beta (r_1 - r_2)^2 .$$

For  $Z = 6 - 8$ , the function  $g(r_1, r_2, r_{12})$  was the same as given above, but  $f(r_1)$  became a simple exponential.

Function III: This was the normalized CI function of STUART and MATSEN<sup>(11)</sup>. The interest in such a wave-function came about indirectly, through a study which was being made of the molecular ion  $\text{HeH}^+$ . (For details, see Part II.) In their paper on  $\text{HeH}^+$  Stuart and Matsen present limited CI functions for the systems He and  $\text{Li}^+$  (which  $\text{HeH}^+$  becomes at  $R = \infty$  and  $R = 0$ , respectively). These functions were included in the present analysis for completeness and to test the correlating ability of a relatively small basis set. They consisted of ten configurations, made up from basis functions which were, as with Weiss, normalized STO's. The basis functions were  $1s$ ,  $2s'$ ,  $3s'$ ;  $2p$ ,  $3p$ ;  $3d$ , giving six (ss) configurations, three (pp) and one (dd). Four independent orbital exponents were used, which were optimized iteratively. Thus this function afforded a nice

comparison with the far more elaborate CI treatment of Weiss.

Function IV: For the "non-correlated" function, relative to which the merits of the correlated functions were examined, the Hartree-Fock function of the form

$$\Psi(1,2) = \phi(r_1) \phi(r_2)$$

was chosen.  $\phi(r_i)$  is the normalized self-consistent field (SCF) function. For the purposes of ease of computation, these SCF orbitals were chosen to be of analytical form. They were, for  $H^-$ , the fitted functions of CURL and COULSON<sup>(12)</sup>, and for He through to  $O^{6+}$ , the "best" SCF functions reported by ROOHTHAAN, SACHS and WEISS<sup>(14)</sup>.

The natural expansion, which has been mentioned earlier and is described in detail in the Appendix, affords a useful way of analysing correlation effects. For atoms, these effects may be classified according to whether they are radial or angular<sup>(15)</sup>. If we constrain two electrons to the same radius vector, the only way they are able to keep apart is by assuming different

(a) Table I p.648 of this paper contains some numerical errors: C.A. Coulson, private communication. Corrections to the analytical SCF wave-function for  $H^-$  have been given by these authors, see ref.(13).

positions along that radius vector; this is known as "radial correlation". Since s-functions are independent of angles, this is the only type of correlation which a wave-function composed of s-functions alone can introduce. (This is the basis of the split-shell technique, DODS, described above.) However, if we instead allow the electrons some angular freedom, they are able to keep apart by so-called "angular correlation". In the main, angular correlation will be introduced if angularly-dependent functions, p, d, etc., are used.

When a CI function is thrown into the form of the natural expansion, the transformation matrix between the two forms is in general block-diagonal. The result of this is that some natural orbitals are composed purely of s-functions, others purely of p-functions, and so on. In the case of Weiss' CI treatment, for example, the natural expansion reduces to fifteen configurations, of which five are composed of s-type orbitals, four of p-type, three of d-type, two of f-type and one of g-type. (Each of these fifteen configurations has, of course, the  $^1S$  symmetry of the ground state of the systems concerned.)

By truncating and re-normalizing the natural expansion it is possible to analyse separately and in more detail the effects of angular and radial correlation. Further explanation of this is given in the next chapter, when the various calculated expectation values are discussed. The results obtained in this

study lend support to the resemblance, noted by other authors<sup>(16,17)</sup>, between the first natural orbital and the Hartree-Fock orbital. Use is made of this apparent similarity during the analysis.

The wave-functions of PEKERIS<sup>(7)</sup> and of FRANKOWSKI and PEKERIS<sup>(18)</sup> were chosen as criteria in this analysis of correlation. Pekeris has produced extremely accurate approximations for H<sup>-</sup>, He and Li<sup>+</sup>, attempting to reach to within 0.001 e.V. of the total nonrelativistic energies of the ground state of these systems. His wave-function depends only on  $r_1, r_2$  and  $r_{12}$ , and is of the form

$$\Psi(1,2) = e^{-\frac{1}{2}(u+v+w)} \sum_{l m n=0}^{\infty} A(l m n) L(u) L(v) L(w)$$

where  $u, v$  and  $w$  are perimetric co-ordinates. The coefficients  $A$  are determined from the wave equation, and the  $L$  are normalized Laguerre polynomials. Pekeris also presents numerous expectation values, and these are taken as the standard when comparison is made with those from the other treatments.

Frankowski and Pekeris have produced very accurate wave-functions for the ground states of the whole two-electron isoelectronic series for  $Z = 1 - 10$ . These were variational calculations containing the unconventional terms  $\ln(r_1 + r_2)$ ,  $[\ln(r_1 + r_2)]^2$  and  $(r_1^2 + r_2^2)^{1/2}$ . The results for these were better than anything published previously, though to the accuracy

required in this present analysis, they agree exactly with those of Pekeris. Consequently we have used the Pekeris results for  $Z = 1 - 3$  and the Frankowski and Pekeris results for  $Z = 4 - 8$ .

Interest in the He and  $\text{Li}^+$  wave-functions arose through the aforementioned study of  $\text{HeH}^+$ . These systems, with the addition of  $\text{H}^-$ , form the beginning of the two-electron series. During the study of these three systems, certain trends seemed to be appearing, and it seemed of interest to extend the study to higher members of the series. For these reasons, the presentation and discussion of the results is in two sections. In Part A,  $\text{H}^-$ , He and  $\text{Li}^+$  are analysed, in some considerable detail. Part B deals with the next five members of the series, though in rather less detail. Hence, the various tables and figures are labelled "A" or "B", depending on which of the two discussion sections they concern.

#### Energies:

Tables I A & B contain, in order of excellence, the total energies obtained from the treatments listed above. The percentage correlation energy is defined in terms of the results of the elaborate calculations by Pekeris and by Frankowski and Pekeris. The "exact" correlation energy has been taken as the difference between the Pekeris and the Hartree-Fock energies. The energies calculated from the first natural orbital  $\chi_1$  of

Weiss and of Stuart and Matsen for the various systems complete the energy tables.

Tables II A & B give the coefficients  $c_i$  associated with the natural orbitals  $\chi_i$  in the natural expansions of the wave-functions of Weiss. Each term in the natural expansion is a configuration of S-type symmetry, composed of basis orbitals whose symmetry-type is represented in the tables by  $\lambda_i$ . This information proves useful later when Table V is discussed in conjunction with Tables II A & B .

CHAPTER 3.

ELECTRON DENSITIES AND EXPECTATION VALUES.

In order to show up the extent and type of correlation which the selected treatments contain, a number of density functions and expectation values were calculated. Taking the results of Pekeris as a standard, comparison was made, where this was possible, between results calculated from the chosen wave-functions and those from Pekeris' work. The various density functions and expectation values are described in some detail below.

Density functions:

It is to be expected that the correlation within a wave-function would have a significant effect on the two-particle radial density distribution  $D(r_1, r_2)$ , which is defined as

$$D(r_1, r_2) = 2 \iint \psi_{(1,2)}^* \psi_{(1,2)} r_1^2 r_2^2 d\Omega_1 d\Omega_2 \quad 3(1)$$

where  $d\Omega_i = \sin\theta_i d\theta_i d\phi_i$  and  $i = 1$  or  $2$ . In these calculations this function is such that

$$\int_0^\infty \int_0^\infty D(r_1, r_2) dr_1 dr_2 = 2. \quad 3(2)$$

Thus, this function is a measure of the probability of the electrons having, simultaneously, radial coordinates in the range  $r_1$  to  $r_1 + dr_1$  and  $r_2$  to  $r_2 + dr_2$ . In particular, in a wave-function which makes allowance for correlation, it is to be expected that the value of  $D(r_1, r_2)$  at  $r_1 = r_2$  would be smaller than that for a non-correlated function, and should itself be small. In order to show up such facts as these, we have drawn maps of the two-particle radial density difference function  $\Delta D(r_1, r_2)$ , which is defined as

$$\Delta D(r_1, r_2) = D(r_1, r_2)_{\text{corr}} - D(r_1, r_2)_{\text{H-F}}, \quad 3(3)$$

i.e. it is the difference between results from a correlated treatment and corresponding results from the best non-correlated treatment; the latter is here represented by the Hartree-Fock approach.

The correlated approach studied here with the best energy was that of Weiss, so  $\Delta D(r_1, r_2)$  maps were drawn using these functions only. Further, it became difficult to represent them on a reasonable scale for  $Z$  greater than 3, which explains why the maps in Fig. 1 are only for  $H^-$ , He and  $Li^+$ . However, these are quite sufficient to show up the incipient trends which occur.

Comparison between the different correlated treatments is demonstrated in Fig. 2. The curves here are of the function

$\Delta D(r_1=r_2)$ , the diagonal of the  $\Delta D(r_1, r_2)$  surface, plotted as a function of  $r_1=r_2$ . All the studied correlated functions are represented in this figure, including those of Stuart and Matsen for He and  $\text{Li}^+$ . From these curves it is possible to compare the relative positions and depths of the minima which occur.

Table III A gives more detailed information than Fig. 2 . It contains the  $(r_1, r_2)$  co-ordinates of the maxima and minima in each  $\Delta D(r_1, r_2)$  surface. Since the differences are of limited value on their own, they are accompanied in Table III A by the absolute values of the Hartree-Fock  $D(r_1, r_2)$ .

The one-particle radial density distribution  $D(r_1)$  is required for the evaluation of several of the expectation values. This function is defined as

$$D(r_1) = \int_0^{\infty} D(r_1, r_2) dr_2 \quad 3(4)$$

and will henceforth simply be referred to as  $D(r)$ . Graphs of  $D(r)$  for the various treatments are shown in Fig. 3 . They show clearly the effects of correlation within the different approximations. Once again, these are only drawn for  $\text{H}^-$ , He and  $\text{Li}^+$  because they become graphically indistinguishable beyond  $Z = 3$ . To assist in the interpretation of these curves, the origins for He and  $\text{Li}^+$  have been displaced.

Expectation values:

Quantum-mechanical averages of  $r^n$ :

These quantities are important because, through their dependence on different regions of the electron density  $D(r)$  they are a guide to the accuracy of a particular approximation. It was mentioned above that the evaluation of certain expectation values requires the function  $D(r)$ . Among these are the  $\langle r^n \rangle$ , where  $-2 \leq n \leq 4$ . They are defined by

$$\langle r^n \rangle = \int D(r) r^n dr \quad . \quad 3(5)$$

This value is clearly the same whichever of the two electrons is specified, so that in this work the values of  $\langle r^n \rangle$  have been calculated to be consistent with the definition

$$\langle r^n \rangle = \langle r_1^n + r_2^n \rangle \quad . \quad 3(6)$$

These average values are useful when estimating how good a certain approximation is at predicting the density in a particular region. Consider, for example,  $r^{-2}$ . This becomes very large near the nucleus. Consequently, the function defined in 3(5) for  $n = -2$  gives a good indication of how well the wavefunction is representing the density in this region. Similarly, the function in 3(5) with  $n = 4$  emphasizes the behaviour of the

wave-function in the far-outer regions. Expectation values of  $r^n$  are presented in Tables IV A & B .

In Chapter 2 it was mentioned that the natural expansion allows a method of analysing separately the effects of radial and angular correlation. Each configuration in the natural expansion for a two-electron atom is composed of basis orbitals of a particular symmetry-type: s, p, d, etc. Thus, starting with the natural expansion truncated to the first configuration (which bears a strong resemblance to the Hartree-Fock function), successive build-up to the total wave-function is equivalent to adding in correlation:- radial from a "radial" configuration of s-orbitals, and angular from an "angular" configuration of p, or d, or f, etc., orbitals. If an expectation value is calculated for each of the successive degrees of truncation, it may clearly be seen how each type of correlation affects that particular expectation value. In the case where the average values are of  $r^n$ , information is given as to how correlation affects  $D(r)$ . Table V contains values of  $\langle r^n \rangle$  calculated for different degrees of truncation of the Weiss CI functions.

Nuclear diamagnetic shielding factor,  $\sigma$  :

When atoms are placed in a homogeneous magnetic field, internal diamagnetic fields are brought about. This was shown by the molecular beam experiments of RABI and his co-workers (19-21) .

A Larmor precession of the electrons takes place and produces at the nucleus a shielding field which is proportional to the external field. The shielding factor is a measure of the extent to which the effective field acting on the nucleus is altered from the external field. Although the effect is small, it is important in measurements of nuclear magnetic moments.

The nuclear diamagnetic shielding factor for atoms and ions is given by <sup>(22,23)</sup>

$$\sigma = \frac{\alpha^3}{3} \langle r^{-1} \rangle \quad 3(7)$$

where  $\alpha$  is Sommerfeld's fine-structure constant.

Atomic diamagnetic susceptibility,  $\chi$  :

The concept of magnetic susceptibility is associated with the interaction between a system and an external homogeneous magnetic field, which induces a magnetic moment in the system. For diamagnetic substances,  $\chi$  is negative and independent of the temperature. With the nucleus as the centre of reference, the diamagnetic susceptibility is given by <sup>(24)</sup>

$$\chi = -0.79199 * 10^{-6} \langle r^2 \rangle \quad 3(8)$$

Because of the  $\langle r^2 \rangle$  - dependence of this quantity, it is a

test of how well a particular approximation represents the density in the outer regions of the atom.

( 26 )

Root-mean-square deviation from the mean,  $\Delta r$ :

This quantity, though strictly speaking not an expectation value, is defined as

$$\Delta r = \left[ \langle r^2 \rangle_{av} - \langle r \rangle_{av}^2 \right]^{1/2}, \quad 3(9)$$

and is thus derived from expectation values.

Here,  $\langle r^2 \rangle_{av} = \langle r^2 \rangle / 2$  and  $\langle r \rangle_{av} = \langle r \rangle / 2$ . Evaluation of this statistical quantity gives a measure of the spread or diffuseness of each  $D(r)$  curve.

Values of  $\sigma$ ,  $\chi$  and  $\Delta r$  are all presented in Tables VI A & B.

X-ray scattering factor,  $f(X)$ :

The scattering of X-rays by an atom is due almost entirely to the electrons in the system. When a monochromatic beam of X-rays is scattered by a gas, the scattered radiation may be observed to be a combination of two components. One of these, the "coherent" part, is characterized by having the same frequency as the incident radiation. The other, the "incoherent" part, arises from the Compton Effect, and has a series of frequencies all lower than that of the incident rays. (This

latter component will not be considered further in this work.)

The atomic scattering factor  $f(X)$  of an atom is the ratio of the amplitude  $A_s$  of the radiation scattered by the atom to the amplitude  $A_e$  which an electron would scatter under the same conditions according to the classical theory (27). In terms of intensities

$$f^2 = I_s / I_e . \quad 3(10)$$

Considering the spherical part of the density, the atomic scattering factor may be defined as

$$f_{00}(X) = \int_0^{\infty} D(r) \frac{\sin 4\pi Xr}{4\pi Xr} dr \quad 3(11)$$

where  $X = \sin \frac{\theta}{2} / \lambda$ .  $\theta$  is the angle of scatter and  $\lambda$  is the wavelength of the radiation.

Graphs have been drawn (see Fig. 4) of  $f_{00}$  as a function of the variable  $X$ . When  $X$  tends to zero,  $f_{00}$  tends to the value  $\int_0^{\infty} D(r) dr$ , the number of electrons in the atom. For large  $X$  values, the scattering curve depends essentially on the inner regions of the density. Thus, considered as a whole, scattering factors are a manifestation of the overall density distribution.

Other expectation values:

The average value of  $\cos \gamma_{12}$ , where  $\gamma_{12}$  is the angle subtended at the nucleus by the electrons, gives a measure of the angular correlation included in a wave-function (15). For a non-correlated wave-function, the average value would be zero, leading to a corresponding value for  $\gamma_{12}$  of  $90^\circ$ . For a correlated wave-function, however, the tendency of the electrons to avoid one another would lead to a value of  $\langle \cos \gamma_{12} \rangle$  such that the corresponding  $\gamma_{12}$  would be greater than  $90^\circ$ . Tables VI A & B contain values of the complete quantum-mechanical average of  $\cos \gamma_{12}$ , while Table III A contains values evaluated at the maxima and minima of the  $\Delta D(r_1, r_2)$  surfaces.

Allied to  $\langle \cos \gamma_{12} \rangle$  is the quantity  $\langle \bar{r}_1 \cdot \bar{r}_2 \rangle$ , which is defined by

$$\langle \bar{r}_1 \cdot \bar{r}_2 \rangle = \langle r_1 r_2 \cos \gamma_{12} \rangle. \quad 3(12)$$

It is required in the investigation of the properties of two-electron systems using the oscillator strength sum rules (28).

The Dirac delta-functions  $\delta^3(\bar{r}_1)$  and  $\delta^3(\bar{r}_{12})$  occur in the evaluation of relativistic corrections to the ground state energy. (29) In addition they are needed in the calculation of certain radiative corrections (30). Their expectation values are

defined by

$$\langle \delta^3(\bar{r}_1) \rangle = \int \Psi^*(\bar{r}_1, 0) \Psi(\bar{r}_1, 0) d\tau_1 \quad 3(13)$$

and

$$\langle \delta^3(\bar{r}_{12}) \rangle = \int \Psi^*(\bar{r}_1, \bar{r}_1) \Psi(\bar{r}_1, \bar{r}_1) d\tau_1 . \quad 3(14)$$

Results for all these expectation values are given in  
Tables VI A & B .

CHAPTER 4.

DISCUSSION OF RESULTS.

For reasons mentioned previously it was found most convenient to present and discuss the results of this work in two sections. The first of these, Part A, deals with  $H^-$ , He and  $Li^+$ , and the second, Part B, with the remaining systems,  $Be^{2+}$  -  $O^{6+}$ , with  $Z = 4 - 8$ .

A.  $H^-$ , He and  $Li^+$ :

The results in Table I A for the total energies of the systems show that the energies from the functions of Weiss and of Green et al are each in very good agreement with the results of Pekeris, each providing a steadily increasing percentage of the Pekeris total energy as  $Z$  increases. Regarding the percentage correlation energy the Weiss results show a steady decrease with increasing  $Z$  and the Green et al values show a larger steady decrease. Each provides a high percentage, however, and even the limited CI treatment of Stuart and Matsen provides around 94% of the correlation energy.

Turning to the energies obtained from the wave-functions truncated to the first natural orbital  $\chi_1$  for the CI expansions of Weiss and of Stuart and Matsen, a strong similarity is seen

to exist between these and the Hartree-Fock energies. This is most noticeable for He and  $\text{Li}^+$ ; for  $\text{H}^-$ , the agreement is not quite as good. The basic limitation, mentioned earlier, of the Hartree-Fock approximation is strikingly illustrated for  $\text{H}^-$ , because its failure to predict a bound state is almost entirely due to its inability to account fully for the correlation of the electrons. These points thus lend support to the findings of other workers <sup>(16,17)</sup> regarding the closeness of  $\chi_1$  and Hartree-Fock energies for two-electron systems. By means of a perturbation expansion, NAZAROFF and HIRSCHFELDER <sup>(31)</sup> have in fact shown that the two orbitals begin to differ from each other in the second order.

Table II A comprises a list of the coefficients  $c_i$  in the natural expansion of the Weiss wave-functions. These coefficients correspond to configurations derived from basis orbitals of symmetry  $\lambda_i$ . In view of the points mentioned above, it seems reasonable to consider the wave-function truncated to the first natural orbital configuration as the "non-correlated" function, so that all succeeding configurations contribute to the correlation in the system. This standpoint will be adopted in this and later discussions.

The  $c_i$  may be considered to provide a measure of the relative importance of configurations composed of basis orbitals of symmetry  $\lambda_i$ . As  $Z$  increases,  $c_1$  increases whilst all the

other coefficients decrease. If all those above the first are to be considered as correlating configurations, then this may be interpreted that correlation effects become relatively less important as  $Z$  increases - a conclusion which may be also reached from the energies in Table I A . Further, the  $c_i$  representing radial configurations show a more rapid decrease with increasing  $Z$  than do those representing angular configurations.

As well as these general trends, however, Table II A allows a clearer insight into the way correlation is introduced into the systems as  $Z$  increases. For  $H^-$ ,  $c_2$  corresponds to a radial configuration, and is considerably larger than  $c_3$ , which corresponds to an angular configuration. For He,  $c_2$  now corresponds to an angular configuration, and is roughly equal to  $c_3$ , which now corresponds to a radial configuration. A similar state of affairs exists for  $Li^+$ , except that  $c_2$  has now become considerably larger than  $c_3$ . This indicates a trend such that in  $H^-$ , the initial introduction of radial correlation is more important than that of angular correlation. The situation becomes reversed for  $Li^+$ , with He representing the transition stage, in which radial and angular correlation are almost equally balanced.

In order to extend this, a measure of the total radial correlation "character" and of the total angular correlation "character" are presented in Table II A . These are, respectively,

the sum of the squares of the  $c_i$  which correspond to radial configurations (other than the first) and the sum of the squares of the  $c_i$  which represent angular configurations. They show a similar switch-over in relative magnitude, with He as the approximate transition point.

The  $\Delta D(r_1, r_2)$  surfaces in Fig. 1 are negative along the diagonal, indicating the anticipated lowering due to correlation of the CI density relative to the Hartree-Fock density for  $r_1=r_2$ . The three surfaces, drawn on the same scale, show the effect of the increasing nuclear charge by being pulled in strongly towards the nucleus. As may be seen from the plots of  $\Delta D(r_1=r_2)$  in Fig. 2, the minima become deeper and closer to the nucleus as  $Z$  increases. Whereas for He and  $\text{Li}^+$  the Weiss functions provide the deepest pair of minima, for  $\text{H}^-$  the results from functions I and II are more closely related. The results from function III for He and  $\text{Li}^+$  fit quite well into the general pattern.

From the more detailed information in Table III A, several interesting points arise. The coordinates of the maxima and minima in  $\Delta D(r_1, r_2)$  for functions I and II are in quite good general agreement. The minima become larger in magnitude as  $Z$  increases, but this quantity expressed as a fraction of the Hartree-Fock value for  $D(r_1=r_2)$  becomes considerably smaller.

A similar trend exists for the maxima. When  $\langle \cos \gamma_{12} \rangle_{r_1, r_2}$  is evaluated at a minimum, i.e.  $r_1 = r_2$ , a more negative value (indicating a larger corresponding  $\gamma_{12}$ ) is obtained than when the evaluation is made at a maximum. Finally, for the maximum of each  $D(r_1, r_2)$  surface, the quantity  $(r_2 - r_1)$  decreases somewhat more rapidly than  $\langle \cos \gamma_{12} \rangle_{r_1, r_2}$  as  $Z$  increases.

Examination of the  $D(r)$  curves in Fig. 3 reveals that as  $Z$  increases, the correlated and non-correlated one-particle radial density distributions soon become indistinguishable, to within graphical accuracy. For  $H^-$ , the Hartree-Fock density is more contracted towards the origin than either of the correlated densities. Though it is not evident from the graphs, a study of the data for He and  $Li^+$  shows a similar effect.

The most obvious trends from the  $\langle r^n \rangle$  values in Table IV A are that, whereas for  $H^-$  the Weiss function gives a slightly more diffuse  $D(r)$  than that obtained from the function of Green et al, the opposite is the case for He and  $Li^+$ . The results from functions I and II show good agreement throughout with those of Pekeris, and those from function III are also quite good by comparison.

Although the  $\langle r^n \rangle$  values for He and  $Li^+$  from the Hartree-Fock functions are in quite good agreement with those from  $\chi_1$

(Weiss), a large discrepancy occurs between these values for  $H^-$ . This may well be connected with the point noticed in the study of Table I A , that the only discrepancy of any size between the energies from the Hartree-Fock and the  $\chi_1$  (Weiss) functions was for  $H^-$ .

From the  $\Delta r$  values also (Table VI A), a large discrepancy between Hartree-Fock and  $\chi_1$  (Weiss) values only occurs for  $H^-$ . A study of the  $\Delta r$  values for functions I and II confirms the trend apparent from the  $\langle r^n \rangle$  values, that whereas for  $H^-$  the Weiss function gives a slightly more diffuse  $D(r)$  than that of Green et al, the opposite is the case for He and  $Li^+$ .

The results in Table V allow examination to be made of changes in  $\langle r^n \rangle$  as correlation effects are gradually introduced into the wave-function. (This table should be studied in conjunction with Table II A , which contains information about the symmetry-type of the basis orbitals composing each configuration in the natural expansion.) Correlation seems to produce the greatest effect in the values for  $H^-$ . Further, the general implication which these values reveal is that within each natural expansion, the inclusion of configurations involving s-orbitals causes  $D(r)$  to become more diffuse, whereas addition of those composed of angular-type orbitals usually results in a contraction. There seems to be no general rule at this stage as to the number of terms required for convergence to the total

value.

The X-ray scattering curves in Fig. 4 become indistinguishable for He and  $\text{Li}^+$ . For  $\text{H}^-$ , the Hartree-Fock curve assumes the same position relative to that for the correlated functions as was found by SILVERMAN, PLATAS and MATSEN<sup>(32)</sup> in a study of the scattering factors produced by various correlated and uncorrelated functions. Included in Fig. 4 are curves for the one-electron systems with the same Z values.

The nuclear diamagnetic shielding factor,  $\sigma$ , and the atomic diamagnetic susceptibility,  $\chi$ , depend on  $\langle r^{-1} \rangle$  and  $\langle r^2 \rangle$ , respectively, so that the values for these quantities in Table VI A follow the same trends as were pointed out earlier for the  $\langle r^n \rangle$  values. HAVENS<sup>(33)</sup> gives experimental values for  $\chi$  for helium of -1.906 at room temperature and -1.91 at liquid air temperature, showing negligible temperature dependence.

Though there are no values for  $\langle \cos \gamma_{12} \rangle$  from Pekeris, comparison of  $\langle \bar{r}_1 \cdot \bar{r}_2 \rangle$  values shows steadily improving agreement between the results from Weiss and those from Pekeris, as Z increases. For the Weiss functions, the values of  $\gamma_{12}$  corresponding to  $\langle \cos \gamma_{12} \rangle$  are: for  $\text{H}^-$ ,  $\gamma_{12} = 96.03^\circ$ ; for He,  $\gamma_{12} = 93.69^\circ$ ; and for  $\text{Li}^+$ ,  $\gamma_{12} = 92.50^\circ$ . The values from Green et al for  $\langle \cos \gamma_{12} \rangle$  and  $\langle \bar{r}_1 \cdot \bar{r}_2 \rangle$  are considerably more negative than

those of Weiss. The Stuart and Matsen values give only poor agreement with those of Pekeris.

Values of the Dirac delta-function  $\delta^3(\bar{r}_1)$  from functions I and II are in reasonable agreement with the Pekeris values, with the Weiss results in general being closer. The  $\chi_1$  (Weiss) values are in poor agreement with the corresponding Hartree-Fock results. The  $\chi_1$  (Stuart and Matsen) and Hartree-Fock values show a much better agreement for  $\delta^3(\bar{r}_{12})$ , whereas the Green et al results show poorer agreement with the Pekeris values with increasing Z.

B. Be<sup>2+</sup>, B<sup>3+</sup>, C<sup>4+</sup>, N<sup>5+</sup>, O<sup>6+</sup>:

The energy values of Frankowski and Pekeris are used as the yardstick in Table I B. The percentage correlation energy supplied by the Weiss functions seems to have reached a steady value of about 98%, whereas the values of Green et al for this quantity show a continued steady decrease. The excellent agreement found in Part A between the energies from the first natural orbital  $\chi_1$  and the Hartree-Fock treatment is seen to be maintained throughout the two-electron series. The effect of neglecting all terms in the natural expansion of the Weiss wave-function other than the first leads to energy differences from the total function of 0.0406 (H<sup>-</sup>), 0.0428 (Li<sup>+</sup>), 0.0440 (B<sup>3+</sup>) and increasing slowly

to 0.0446 ( $O^{6+}$ ). The "exact" correlation energy has values 0.0398 ( $H^-$ ), 0.0435 ( $Li^+$ ), 0.0448 ( $B^{3+}$ ) through to 0.0454 ( $O^{6+}$ ).

The coefficients in Table II B show a continuance of the trends developed by those in Table II A. All above  $c_1$  decrease with increasing  $Z$ , and those corresponding to radial configurations decrease more rapidly than those representing angular configurations. An assessment of the total radial and total angular correlation "character" is again included.

From Table III B, it can be seen that the minima in  $\Delta D(r_1=r_2)$  become deeper and closer to the nucleus as  $Z$  increases, though their depths as a fraction of the Hartree-Fock values for  $D(r_1=r_2)$  become considerably smaller. Similar features occur for the maxima. All these trends are in accord with those from Part A. Fig. 5 illustrates graphically the variation in the magnitudes of the maxima and minima as  $Z$  increases.

The  $\langle r^n \rangle$  values for  $\chi_1$  and the Hartree-Fock functions are generally close, but deeper examination reveals the following pattern. For  $\langle r^{-2} \rangle$  and  $\langle r^{-1} \rangle$ , the  $\chi_1$  values are consistently larger than the Hartree-Fock results, whereas they are lower for larger values of  $n$ . Referring back to Part A, a similar trend existed for  $Li^+$  although the change-over occurred, not at  $\langle r^{-1} \rangle$  but at  $\langle r^3 \rangle$ . For He and  $H^-$ , however, the  $\chi_1$  values are always larger than the Hartree-Fock values.

A study of the  $\langle r^n \rangle$  values from truncated natural expansions

again shows that the corresponding  $D(r)$  expand when configurations involving s-orbitals are added in. The effect rapidly decreases, however, as  $Z$  increases, and for this reason details are not given. The effect of angular configurations was less clear cut. In parentheses in Table IV B are the number of terms required in the natural expansion for convergence to the total  $\langle r^n \rangle$  value to be reached. These now show that the number of terms tends to decrease with increasing  $Z$ .

Table VII contains values of the one-particle density  $\rho(\bar{r})$  at the nucleus for the CI wave-function of Weiss and the Hartree-Fock function. The values for the former are consistently higher than for the non-correlated function - an effect similar to that found in a simple molecule, see Part II - for all values of  $Z$ . Except for  $H^-$ , the percentage change with respect to the Hartree-Fock result is small, and decreases markedly with increasing atomic number.

The values of  $\langle \cos \gamma_{12} \rangle$  from the Weiss functions, in Table VIB, show the trend continuing from Part A. The corresponding values of  $\gamma_{12}$  are :  $Be^{2+}$   $91.89^\circ$ ,  $B^{3+}$   $91.51^\circ$ ,  $C^{4+}$   $91.26^\circ$ ,  $N^{5+}$   $91.08^\circ$  and  $O^{6+}$   $90.95^\circ$ . The values from Green et al for  $\langle \cos \gamma_{12} \rangle$  and  $\langle \bar{r}_1 \cdot \bar{r}_2 \rangle$  are again rather more negative than the corresponding Weiss results.

In a paper on the properties of the helium isoelectronic sequence, DALGARNO and STEWART <sup>(30)</sup> use perturbation calculations,

and give formulae for the quantities  $\langle \bar{r}_1 \cdot \bar{r}_2 \rangle$  and  $\chi$ . These formulae are

$$\langle \bar{r}_1 \cdot \bar{r}_2 \rangle = -\frac{0.379}{z^3} - \frac{0.240}{z^4} ,$$

$$\chi = -0.79199 \left[ \frac{6}{z^2} + \frac{4.78125}{z^3} + \frac{4.35616}{z^4} \right] .$$

Using these we have calculated values for  $\langle \bar{r}_1 \cdot \bar{r}_2 \rangle$  and  $\chi$ , and these are contained in brackets in Table VI B, below the corresponding Weiss results. For  $Z = 1 - 3$ , the results are as follows, with the Weiss value first in each case:

$\langle \bar{r}_1 \cdot \bar{r}_2 \rangle$	H <sup>-</sup>	-0.676 ,	-0.619 .
	He	-0.0646,	-0.0624.
	Li <sup>+</sup>	-0.0172,	-0.0170.
$\chi$	H <sup>-</sup>	-18.85 ,	-12.0 .
	He	-1.839 ,	-1.878 .
	Li <sup>+</sup>	-0.707 ,	-0.711 .

Thus, the high accuracy which Dalgarno and Stewart expected from their inverse-Z expansions is well justified, except in the case of the lowest Z values.

CHAPTER 5.

SUMMARY AND CONCLUSIONS.

The analysis presented in the previous pages allows some remarks to be made about the particular methods of approximation which were studied and about the way they represent the correlation in the systems.

The energy tables presented show that both the configuration interaction and the explicitly correlated functions give a good account of the electron correlation and give high percentages of the Pekeris "exact" energy. Even the limited CI, function III, is able to give a reasonably high percentage of the correlation energy.

These tables also show evidence which gives strong support to the results of other workers as regards the similarity between the Hartree-Fock orbital and the first natural orbital for two-electron systems. The only discrepancy of any size in the energies from each of these is for  $H^-$ . The expectation values calculated from each approximation are also in general close together, and this similarity tends to improve for larger values of  $Z$ . This is particularly noticeable for  $\langle r^n \rangle$ , where, for  $H^-$ , there is a large difference between their

respective values for larger values of  $n$ . These results imply a  $Z$ -dependence of the difference between the Hartree-Fock orbital and the first natural orbital, in the sense that the discrepancy decreases with increasing  $Z$ .

There is a certain amount of evidence in our results which indicates that, as  $Z$  increases along the series, angular correlation replaces radial correlation as being more important. For instance, the natural orbital coefficients show that, initially at least, radial correlation is more important in  $H^-$  but angular correlation becomes dominant to a greater and greater extent as we move up the series. The total correlation "character" is also largely radial for  $H^-$ , but this again soon changes to angular and becomes increasingly so. Although each of the  $c_i$  (for  $i > 1$ ) decreases as  $Z$  increases, the ones which represent angular configurations decrease slower than those which represent radial configurations. Thus, while correlation as a whole becomes relatively less important, angular correlation decreases more slowly than radial.

Further, from the  $\Delta D(r_1, r_2)$  surfaces we saw that the maxima and minima had magnitudes which became smaller and smaller percentages of the corresponding Hartree-Fock values. These effects could be explained by saying that the increasing nuclear charge shows its effect by inhibiting the radial freedom of the electrons, hence causing a relative increase in

correlation by means of angular separation.

The  $\langle r^n \rangle$  values calculated as a function of truncation of the natural expansion show that, in general,  $D(r)$  becomes more diffuse when a radial configuration is introduced, whereas an angular configuration generally contracts it. These conclusions are in accord with those of GODDARD <sup>(34)</sup>.

The expectation values calculated from the Weiss CI functions generally have good agreement with those of Pekeris. This is especially true for  $\langle \bar{r}_1, \bar{r}_2 \rangle$  values. The results of Green et al are also good by comparison with Pekeris for lower Z values, but they become rather erratic for higher atomic numbers. In particular, the values of  $\langle \cos \gamma_{12} \rangle$  and  $\langle \bar{r}_1, \bar{r}_2 \rangle$  seem rather too negative, suggesting that the correlation factors contained in these wave-functions over-estimate the importance of angular correlation. Also, as indicated by the  $\Delta r$  values, the density seems to become over-diffuse with respect to Pekeris, as Z increases.

The curves of the X-ray scattering factors showed that changes due to correlation effects were small, as Z increased. The agreement between  $f_{00}(X)$  for  $H^-$  and the H atom at large X is good, but this agreement is not apparent for He and  $Li^+$ . Thus, though for  $H^-$  it might be conjectured that the "inner" correlated electron was in a state similar to that for the one-electron atom, this does not seem to carry over to systems

with higher Z values. In general, we tend to agree with RUSTGI  
(35)  
and TIWARI that it is not possible to extract any  
reliable information on the angular and radial correlation of  
electrons from the scattering factors.

The general agreement for  $\chi$  and  $\langle \bar{r}_1, \bar{r}_2 \rangle$  between the  
Weiss results and those from the expansions of Dalgarno and  
Stewart is good except for low Z values. This is an expected  
result, in view of the inevitable slow convergence of their  
inverse-Z expansions for such values.

Wavefunction	$H^-$		He		$Li^+$	
	Energy -E (a.u.)	% corr. (a)	Energy -E (a.u.)	% corr. (a)	Energy -E (a.u.)	% corr. (a)
I - Weiss (35-C.I.) <sup>(b)</sup>	0.5275	99.2	2.9032	98.8	7.2792	98.4
II - Green et al. <sup>(c)</sup> ( $r_{12}$ )	0.5273	98.7	2.9026	97.4	7.2781	95.9
III - S. and M. <sup>(d)</sup> (10-C.I.)			2.9015	94.8	7.2771	93.6
IV - Hartree-Fock <sup>(e)</sup>	0.4880	0 <sup>(h)</sup>	2.8617	0 <sup>(h)</sup>	7.2364	0 <sup>(h)</sup>
$x_1$ (Weiss) <sup>(f)</sup>	0.4869		2.8617		7.2364	
$x_1$ (S. and M.) <sup>(f)</sup>			2.8616		7.2364	
Pekeris <sup>(g)</sup>	0.5278	100 <sup>(h)</sup>	2.9037	100 <sup>(h)</sup>	7.2799	100 <sup>(h)</sup>

Table IA . Wave-functions and Energies, Z = 1-3.

(a) % correlation =  $100 \left[ \frac{[E - E_{H-F}]}{[E_{Pekeris} - E_{H-F}]} \right]$  .

(b) Reference 8 .

(c) Reference 10 .

(d) Reference 11 .

(e) Reference 14 .

(f) First natural orbitals in the appropriate natural expansion.

(g) Reference 7 .

(h) By definition.

Z	System	4	5	6	7	8
Wavefunction	Be <sup>2+</sup>	B <sup>3+</sup>	C <sup>4+</sup>	N <sup>5+</sup>	O <sup>6+</sup>	
	Energy -E (a.u.)					
	% corr. (a)					
I - Weiss (35-C.I.) <sup>(b)</sup>	13.6548	22.0302	32.4054	44.7806	59.1557	98.0
II - Green et al. <sup>(c)</sup> (r <sub>12</sub> )	13.6533	22.0284	32.4034	44.7785	59.1535	93.2
IV - Hartree-Fock <sup>(d)</sup>	13.6113	21.9862	32.3612	44.7362	59.1112	0 <sup>(g)</sup>
x <sub>1</sub> (Weiss) <sup>(e)</sup>	13.6113	21.9862	32.3612	44.7362	59.1111	...
Frankowski <sup>(f)</sup> and Pekeris	13.6556	22.0310	32.4062	44.7814	59.1566	100 <sup>(g)</sup>

Table IB . Wave-functions and Energies, Z = 4-8.

(a) % correlation =  $100 \left[ \frac{E - E_{H-F}}{E_{Pekeris} - E_{H-F}} \right]$  .

(b) Reference 8 .

(c) Reference 10 .

(d) Reference 14 .

(e) First natural orbitals in the appropriate natural expansion .

(f) Reference 18 .

(g) By definition .

$\chi_i$	$\text{H}^-$		$\text{He}$		$\text{Li}^+$	
	$c_i$	$\lambda_i$	$c_i$	$\lambda_i$	$c_i$	$\lambda_i$
1	-0.97152	(s)	-0.99598	(s)	-0.99840	(s)
2	0.20768	(s)	0.06191	(p)	0.04149	(p)
3	0.11000	(p)	0.06163	(s)	0.03691	(s)
4	0.01775	(d)	0.01265	(d)	0.00903	(d)
5	0.01574	(p)	0.01114	(p)	0.00779	(p)
6	0.01411	(s)	0.00790	(s)	0.00521	(s)
7	0.00585	(f)	0.00448	(f)	0.00326	(f)
8	0.00511	(d)	0.00390	(d)	0.00280	(d)
9	0.00376	(p)	0.00328	(p)	0.00230	(p)
10	0.00330	(s)	0.00192	(s)	0.00131	(s)
11	0.00250	(g)	0.00180	(g)	0.00129	(g)
12	0.00205	(f)	0.00160	(f)	0.00115	(f)
13	0.00181	(d)	0.00132	(d)	0.00091	(d)
14	0.00161	(p)	0.00087	(p)	0.00055	(p)
15	0.00005	(s)	0.00065	(s)	0.00044	(s)
$\sum_{i \neq 1} c_i^2 (\lambda_i = s)$	0.04334		0.00386		0.00139	
$\sum_i c_i^2 (\lambda_i \neq s)$	0.01276		0.00417		0.00189	

Table II A . Coefficients  $c_i$ , and symmetry  $\lambda_i$  of the basis orbitals, associated with each  $\chi_i$  in the natural expansion of the Weiss CI wave-functions,  $Z = 1-3$ .

Z $\chi_i$	4 Be <sup>2+</sup>		5 B <sup>3+</sup>		6 C <sup>4+</sup>		7 N <sup>5+</sup>		8 O <sup>6+</sup>	
	$c_i$	$\lambda_i$	$c_i$	$\lambda_i$	$c_i$	$\lambda_i$	$c_i$	$\lambda_i$	$c_i$	$\lambda_i$
1	-0.99916	(s)	-0.99947	(s)	-0.99967	(s)	-0.99978	(s)	-0.99984	(s)
2	0.03112	(p)	0.02489	(p)	0.02072	(p)	0.01775	(p)	0.01554	(p)
3	0.02637	(s)	0.02052	(s)	0.01679	(s)	0.01422	(s)	0.01233	(s)
4	0.00694	(d)	0.00564	(d)	0.00476	(d)	0.00409	(d)	0.00361	(d)
5	0.00594	(p)	0.00479	(p)	0.00400	(p)	0.00346	(p)	0.00303	(p)
6	0.00388	(s)	0.00309	(s)	0.00256	(s)	0.00219	(s)	0.00191	(s)
7	0.00254	(f)	0.00201	(f)	0.00172	(f)	0.00150	(f)	0.00131	(f)
8	0.00215	(d)	0.00174	(d)	0.00147	(d)	0.00127	(d)	0.00112	(d)
9	0.00175	(p)	0.00140	(p)	0.00117	(p)	0.00101	(p)	0.00088	(p)
10	0.00099	(s)	0.00081	(s)	0.00067	(s)	0.00058	(s)	0.00050	(s)
11	0.00098	(g)	0.00080	(g)	0.00066	(g)	0.00057	(g)	0.00049	(g)
12	0.00089	(f)	0.00065	(f)	0.00056	(f)	0.00049	(f)	0.00044	(f)
13	0.00068	(d)	0.00054	(d)	0.00045	(d)	0.00039	(d)	0.00034	(d)
14	0.00040	(p)	0.00031	(p)	0.00026	(p)	0.00021	(p)	0.00019	(p)
15	0.00034	(s)	0.00028	(s)	0.00023	(s)	0.00020	(s)	0.00017	(s)
$\sum_{i \neq 1} c_i^2 (\lambda_i = s)$	0.00070		0.00043		0.00028		0.00021		0.00015	
$\sum_i c_i^2 (\lambda_i = s)$	0.00106		0.00068		0.00047		0.00035		0.00027	

**Table II B .** Coefficients  $c_i$ , and symmetry  $\lambda_i$  of the basis orbitals, associated with each  $\chi_i$  in the natural expansion of the Weiss wave-functions,  $Z = 4-8$ .

System	Wavefunction	Maxima				Minima				
		$r_1$	$r_2$	$\Delta D(r_1, r_2)$	$D(r_1, r_2)$	$\langle \cos \gamma \rangle_{r_1, r_2}$	$r_1 - r_2$	$\Delta D(r_1, r_2)$	$D(r_1, r_2)$	$\langle \cos \gamma \rangle_{r_1, r_2}$
$H^-$	I - Weiss (a)	0.84	4.26	0.02737	0.04833	-0.04548	0.97	-0.08307	0.19128	-0.12553
	II - Green et al	0.80	4.01	0.02778	0.05444	-0.05486	0.93	-0.08408	0.18476	-0.12281
He	I - Weiss (a)	0.37	1.36	0.07521	0.54520	-0.03521	0.37 1.29	-0.17833 -0.03311	1.12003 0.33383	-0.05615 -0.12267
	II - Green et al	0.36	1.40	0.07088	0.50059	-0.04532	0.37 1.33	-0.17330 -0.03122	1.12003 0.29310	-0.05062 -0.13307
	III - S. and M.	0.36	1.41	0.07628	0.49214	-0.01914	0.37 1.30	-0.16884 -0.03504	1.12003 0.32323	-0.03023 -0.07357
$Li^+$	I - Weiss (a)	0.23	0.83	0.12217	1.47107	-0.02385	0.23 0.81	-0.28029 -0.05438	2.81999 0.85532	-0.03622 -0.08222
	II - Green et al	0.24	0.86	0.10736	1.39280	-0.03360	0.23 0.82	-0.26421 -0.05233	2.81999 0.81037	-0.03129 -0.09136
	III - S. and M.	0.23	0.86	0.12123	1.35368	-0.01373	0.23 0.82	-0.26575 -0.05591	2.81999 0.81037	-0.01941 -0.04846

Table III A. Maxima and minima in the  $\Delta D(r_1, r_2)$  surfaces,  $Z = 1-3$ .

(a) See Fig. 1 for contour maps of  $\Delta D(r_1, r_2)$  for the Weiss functions.

System	Maxima				Minima		
	$r_1$	$r_2$	$\Delta D(r_1, r_2)$	$D(r_1, r_2)_{IV}$	$r_1 = r_2$	$\Delta D(r_1 = r_2)$	$D(r_1 = r_2)_{IV}$
4 $Be^{2+}$	0.18	0.60	0.16798	2.96398	0.16 0.58	-0.38410 -0.07606	4.96692 1.74415
5 $B^{3+}$	0.14	0.46	0.21534	5.04726	0.14 0.46	-0.48429 -0.09774	9.35218 2.72393
6 $C^{4+}$	0.12	0.38	0.26033	7.58689	0.10 0.38	-0.58485 -0.11935	11.14324 3.97193
7 $N^{5+}$	0.08	0.32	0.29951	8.91667	0.10 0.32	-0.68493 -0.14110	19.56631 5.74086
8 $O^{6+}$	0.08	0.28	0.35607	13.05398	0.08 0.28	-0.80293 -0.16366	23.04324 7.39508

Table III B. Maxima and minima in the  $\Delta D(r_1, r_2)$  surfaces for the Weiss functions,  $Z = 4-8$ .

System	Wavefunction	$\langle r^{-2} \rangle$	$\langle r^{-1} \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^3 \rangle$	$\langle r^4 \rangle$
$H^-$	I - Weiss	2.2345	1.3656	5.4243	23.792	150.25	1243.8
	II - Green et al	2.2412	1.3683	5.3846	23.412	147.61	1231.9
	IV - Hartree Fock	2.1596	1.3694	5.0441	19.394	105.57	771.16
	$\chi_1$ (Weiss)	2.2125	1.3693	5.3009	22.501	137.98	1117.9
	Pekeris <sup>(a)</sup>			5.4204	23.827		
He	I - Weiss	12.037	3.3764	1.8587	2.3843	3.9212	7.8759
	II - Green et al	12.025	3.3754	1.8592	2.3871	3.9312	7.9105
	III - S. and M.	12.043	3.3784	1.8574	2.3787	3.8950	7.7594
	IV - Hartree Fock	11.991	3.3744	1.8544	2.3696	3.8811	7.7756
	$\chi_1$ (Weiss)	12.043	3.3795	1.8546	2.3722	3.8889	7.7867
	$\chi_1$ (S. and M.)	12.022	3.3785	1.8543	2.3685	3.8683	7.6903
	Pekeris <sup>(a)</sup>	12.035	3.3766	1.8589	2.3870		
$Li^+$	I - Weiss	29.858	5.3757	1.1455	0.89215	0.88117	1.0551
	II - Green et al	29.822	5.3722	1.1450	0.89295	0.88415	1.0631
	III - S. and M.	29.878	5.3778	1.1449	0.89080	0.87794	1.0473
	IV - Hartree Fock	29.811	5.3716	1.1440	0.89036	0.87865	1.0521
	$\chi_1$ (Weiss)	29.870	5.3781	1.1445	0.89041	0.87845	1.0507
	$\chi_1$ (S. and M.)	29.860	5.3780	1.1442	0.88943	0.87576	1.0438
	Pekeris <sup>(a)</sup>			1.1456	0.89256		

Table IV A . Values of  $\langle r^n \rangle$  ,  $Z = 1-3$ .

(a) Reference 7 .

Z	Wavefunction System	$\langle r^{-2} \rangle$	$\langle r^{-1} \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^3 \rangle$	$\langle r^4 \rangle$
4	Weiss (a)	55.686 (4)	7.3755 (4)	0.82852 (5)	0.46400 (6)	0.32811 (6)	0.28044 (6)
	Hartree-Fock (Weiss)	55.649	7.3748	0.82827	0.46365	0.32780	0.28029
5	Weiss (a)	89.517 (6)	9.3754 (5)	0.64909 (6)	0.28308 (5)	0.15641 (5)	0.10400 (5)
	Hartree-Fock (Weiss)	89.476	9.3749	0.64897	0.28376	0.15634	0.10399
6	Weiss (a)	131.34 (3)	11.375 (2)	0.53358 (6)	0.19145 (3)	0.08641 (3)	0.04702 (3)
	Hartree-Fock (Weiss)	131.31	11.375	0.53351	0.19140	0.08639	0.04703
7	Weiss (a)	181.17 (3)	13.375 (2)	0.45298 (5)	0.13779 (3)	0.05268 (6)	0.02426 (3)
	Hartree-Fock (Weiss)	181.14	13.375	0.45294	0.13777	0.05267	0.02426
8	Weiss (a)	239.00 (3)	15.375 (2)	0.39354 (5)	0.10390 (3)	0.03445 (3)	0.01375 (3)
	Hartree-Fock (Weiss)	238.98	15.375	0.39351	0.10389	0.03445	0.01376
		239.02	15.376	0.39349	0.10387	0.03443	0.01374

Table IV B . Values of  $\langle r^n \rangle$ , Z = 4-8.

(a) The figures in parentheses represent the number of terms in the natural expansion required for convergence to the recorded CI values.

m	H <sup>-</sup>				He				Li <sup>+</sup>			
	< r <sup>-2</sup> >	< r <sup>-1</sup> >	< r <sup>2</sup> >	< r <sup>4</sup> >	< r <sup>-2</sup> >	< r <sup>-1</sup> >	< r <sup>2</sup> >	< r <sup>4</sup> >	< r <sup>-2</sup> >	< r <sup>-1</sup> >	< r <sup>2</sup> >	< r <sup>4</sup> >
1(b)	2.21247	1.36927	22.501	1117.9	12.043	3.37951	2.37219	7.78669	29.870	5.37810	0.89042	1.05071
2	2.25396	1.37064	23.880	1256.0	12.010	3.37547	2.37317	7.78068	29.834	5.37520	0.89066	1.05053
3	2.23394	1.36561	23.793	1244.1	12.038	3.37657	2.38391	7.87247	29.859	5.37587	0.89206	1.05490
4	2.23339	1.36547	23.790	1243.7	12.036	3.37638	2.38393	7.87195	29.858	5.37571	0.89207	1.05488
5	2.23320	1.36547	23.789	1243.5	12.036	3.37633	2.38409	7.87281	29.857	5.37567	0.89210	1.05495
6	2.23448	1.36563	23.793	1243.9	12.037	3.37642	2.38427	7.87498	29.858	5.37572	0.89213	1.05508
7	2.23441	1.36562	23.792	1243.8	12.037	3.37639	2.38427	7.87490	29.858	5.37570	0.89213	1.05508
8	2.23438	1.36561	23.792	1243.8	12.037	3.37638	2.38428	7.87491	29.858	5.37569	0.89213	1.05508
9	2.23439	1.36562	23.792	1243.8	12.037	3.37638	2.38431	7.87514	29.858	5.37569	0.89214	1.05510
10	2.23452	1.36563	23.792	1243.8	12.037	3.37638	2.38435	7.87587	29.858	5.37569	0.89215	1.05514
11	2.23451	1.36563	23.792	1243.8	12.037	3.37638	2.38435	7.87585	29.858	5.37569	0.89215	1.05514
12	2.23450	1.36563	23.792	1243.8	12.037	3.37638	2.38435	7.87584	29.858	5.37569	0.89215	1.05514
13	2.23450	1.36563	23.792	1243.8	12.037	3.37638	2.38435	7.87584	29.858	5.37569	0.89215	1.05514
14	2.23450	1.36563	23.792	1243.8	12.037	3.37638	2.38435	7.87585	29.858	5.37569	0.89215	1.05514
15	2.23450	1.36563	23.792	1243.8	12.037	3.37638	2.38435	7.87590	29.858	5.37569	0.89215	1.05514

Table V . Values of selected  $\langle r^n \rangle$  , obtained from the natural expansions of the Weiss wave-functions, truncated after m terms. The convergence value for each  $\langle r^n \rangle$  is indicated by the dotted line. Each expansion consisted of a total of 15 configurations.

(b) The symmetry  $\lambda_i$  for the basis orbitals associated with each additional configuration included in the truncated expansion is obtained by inspection of Table II A .

System	Wavefunction	$\sigma \times 10^5$	$\chi^{(a)}$	$\Delta r$	$\langle \cos \gamma_{12} \rangle$	$\langle \bar{r}_1 \cdot \bar{r}_2 \rangle$	$\langle \delta^3(F_1) \rangle$	$\langle \delta^3(F_{12}) \rangle$
H <sup>-</sup>	I - Weiss	2.4240	-18.850	2.1308	-0.10500	-0.67622	0.16555	
	II - Green et al	2.4287	-18.549	2.1113	-0.10958	-0.72913	0.16672	0.2984 x 10 <sup>-2</sup>
	IV - Hartree-Fock	2.4307	-15.366	1.8265	(c)	(c)	0.15464	1.2984 x 10 <sup>-2</sup>
	$\chi_1$ (Weiss)	2.4305	-17.828	2.0557	(c)	(c)	0.16168	
	Pekeris <sup>(b)</sup>		-18.878	2.1374		-0.68731	0.16455	0.2742 x 10 <sup>-2</sup>
He	I - Weiss	5.9931	-1.8891	0.57315	-0.06431	-0.06455	1.81558	
	II - Green et al	5.9913	-1.8913	0.57391	-0.07188	-0.07549	1.80926	0.11717
	III and M.	5.9967	-1.8846	0.57167	-0.03768	-0.03724	1.80949	0.14288
	IV - Hartree-Fock	5.9896	-1.8774	0.57014			1.79821	0.19093
	$\chi_1$ (Weiss)	5.9987	-1.8759	0.57113			1.81465	
	$\chi_1$ (S. and M.)	5.9969	-1.8765	0.56978			1.80092	0.19143
Pekeris <sup>(b)</sup>	5.9936	-1.8912	0.57408		-0.06474	1.81043	0.10635	
Li <sup>+</sup>	I - Weiss	9.5419	-0.70685	0.34358	-0.04367	-0.01717	6.86218	
	II - Green et al	9.5457	-0.70749	0.34459	-0.04957	-0.02080	6.83225	0.57492
	III - S. and M.	9.5457	-0.70578	0.34306	-0.02545	-0.00986	6.86207	0.64537
	IV - Hartree-Fock	9.5347	-0.70543	0.34347			6.83702	0.77935
	$\chi_1$ (Weiss)	9.5462	-0.70548	0.34314			6.86291	
	$\chi_1$ (S. and M.)	9.5461	-0.70470	0.34265			6.85040	0.77170
	Pekeris <sup>(b)</sup>		-0.70718	0.34382		-0.01725	6.85199	0.53389

Table VI A . Some expectation values, Z = 1-3.

(a) Reference 25 .

(b) Reference 7 .

(c) Due to the independent particle nature of the Hartree-Fock treatment, and to the fact that  $\chi_1$  is composed of s-type orbitals, this quantity is identically zero.

Z System	Wavefunction	$\Delta r$	$\sigma \times 10^5$	$x^{(a)}$	$\langle \cos \gamma_{12} \rangle$	$\langle \bar{r}_1 \cdot \bar{r}_2 \rangle$
4 $Be^{2+}$	I - Weiss	0.24574	13.0915	--36714 (--36976) <sup>(b)</sup>	--03292	--00686 (--00686) <sup>(b)</sup>
	II - Green et al	0.25166	12.8576	--38342	--04273	--00997
	I - Hartree-Fock	0.24560	13.0903	--36734	(c)	(c)
	(Weiss)	0.24558	13.0949	--36724	(c)	(c)
5 $B^{3+}$	I - Weiss	0.19136	16.6413	--22491 (--22596)	--02641	--00340 (--00342)
	II - Green et al	0.19720	16.3117	--23671	--03470	--00513
	I - Hartree-Fock	0.19131	16.6404	--22482	...	...
	(Weiss)	0.19128	16.6442	--22477	...	...
6 $C^{4+}$	I - Weiss	0.15668	20.1906	--15168 (--15223)	--02203	--00193 (--00194)
	II - Green et al	0.15032	20.1103	--15333	--02810	--00278
	I - Hartree-Fock	0.15668	20.1906	--15164	...	...
	(Weiss)	0.15665	20.1924	--15162	...	...
7 $N^{5+}$	I - Weiss	0.13266	23.7406	--10916 (--10947)	--01890	--00119 (--00120)
	II - Green et al	0.13391	23.6625	--11050	--02379	--00173
	I - Hartree-Fock	0.13266	23.7406	--10915	...	...
	(Weiss)	0.13266	23.7424	--10913	...	...
8 $O^{6+}$	I - Weiss	0.11506	27.2906	--08231 (--08250)	--01657	--00079 (--00080)
	II - Green et al	0.11587	27.2143	--08313	--02079	--00115
	I - Hartree-Fock	0.11502	27.2906	--08231	...	...
	(Weiss)	0.11502	27.2924	--08229	...	...

Table VI B. Some expectation values, Z = 4-8.

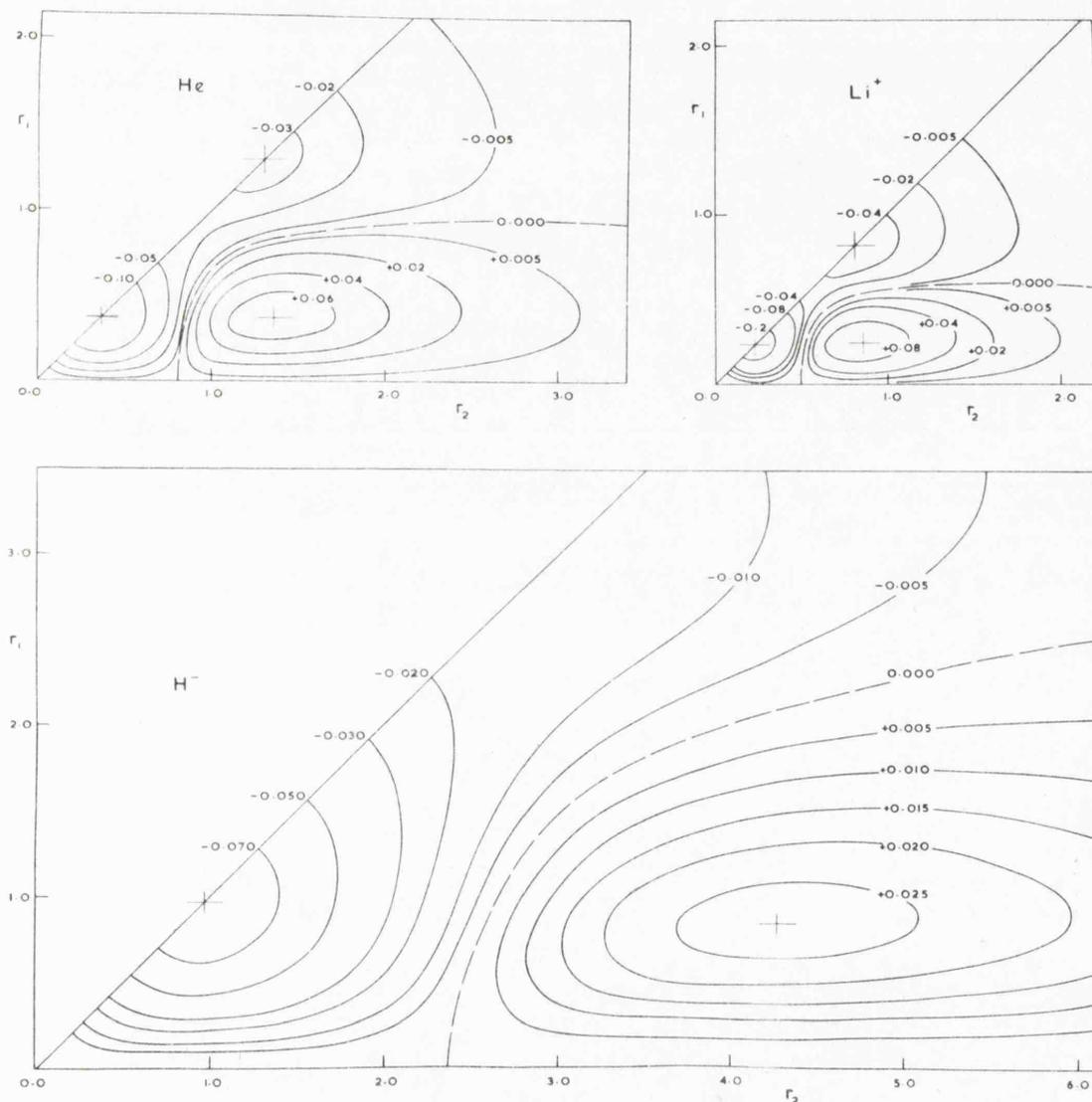
(a) Reference 25.

(b) The figures in parentheses are derived from the inverse-Z expansions of Dalgarno & Stewart.

(c) Due to the independent particle nature of the Hartree-Fock treatment, and to the fact that  $\chi_1$  is composed of s-type orbitals, this quantity is identically zero.

Z	System	Weiss	Green et al	Hartree-Fock
1	H <sup>-</sup>	0.33107	0.33342	0.30913
2	He	3.63124	3.61853	3.59627
3	Li <sup>+</sup>	13.7332	13.6669	13.6732
4	Be <sup>2+</sup>	34.4338	32.7607	34.3585
5	B <sup>3+</sup>	69.5780	66.2518	69.4564
6	C <sup>4+</sup>	122.964	121.805	122.825
7	N <sup>5+</sup>	198.434	196.793	198.242
8	O <sup>6+</sup>	299.805	297.660	299.609

Table VII . Density  $\rho(\bar{r})$  evaluated at the nucleus.



**Fig. 1** . Maps of the two-particle radial density difference  $\Delta D(r_1, r_2)$  for  $H^-$ , He and  $Li^+$ . These are obtained by subtracting the two-particle radial density  $D(r_1, r_2)$  for the Hartree-Fock functions from the corresponding values for the Weiss functions.

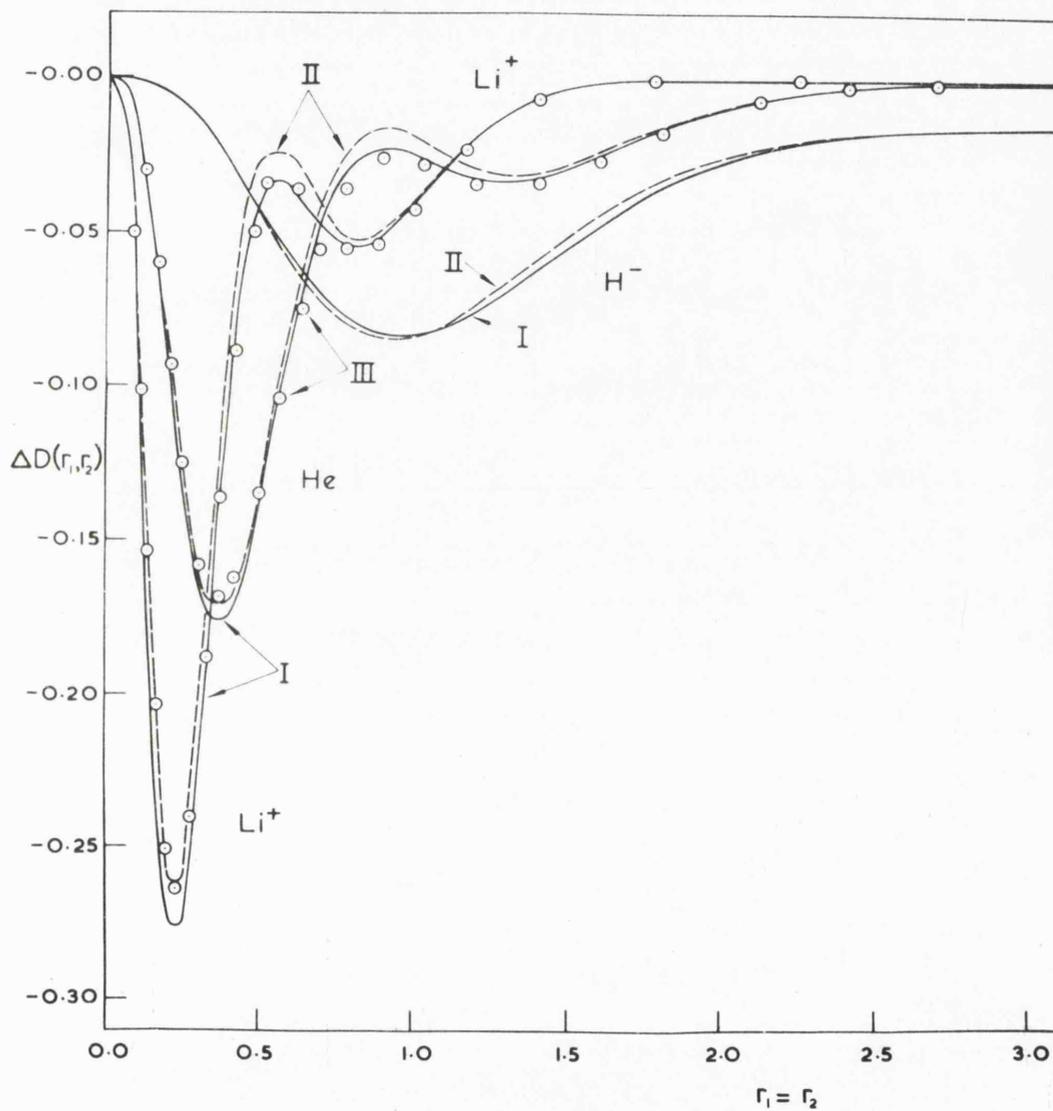
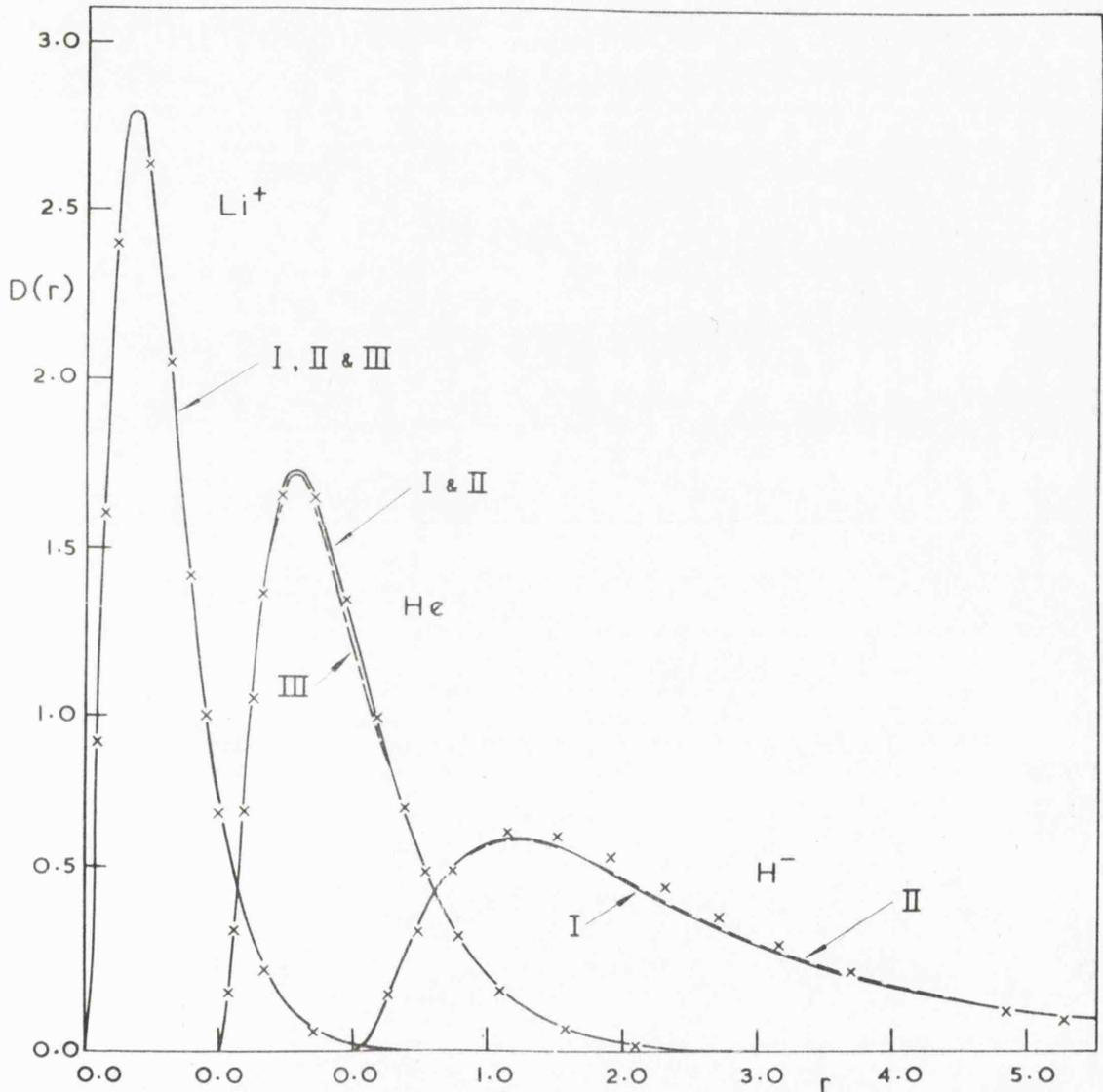
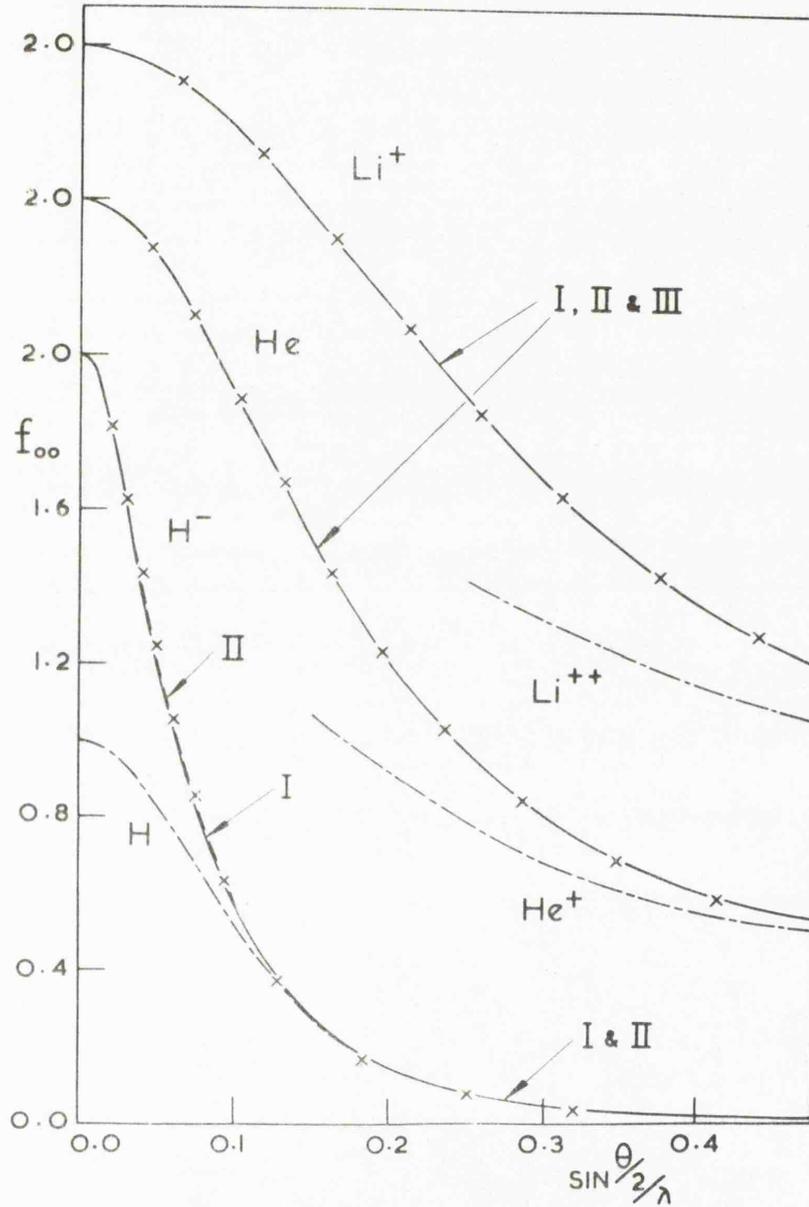


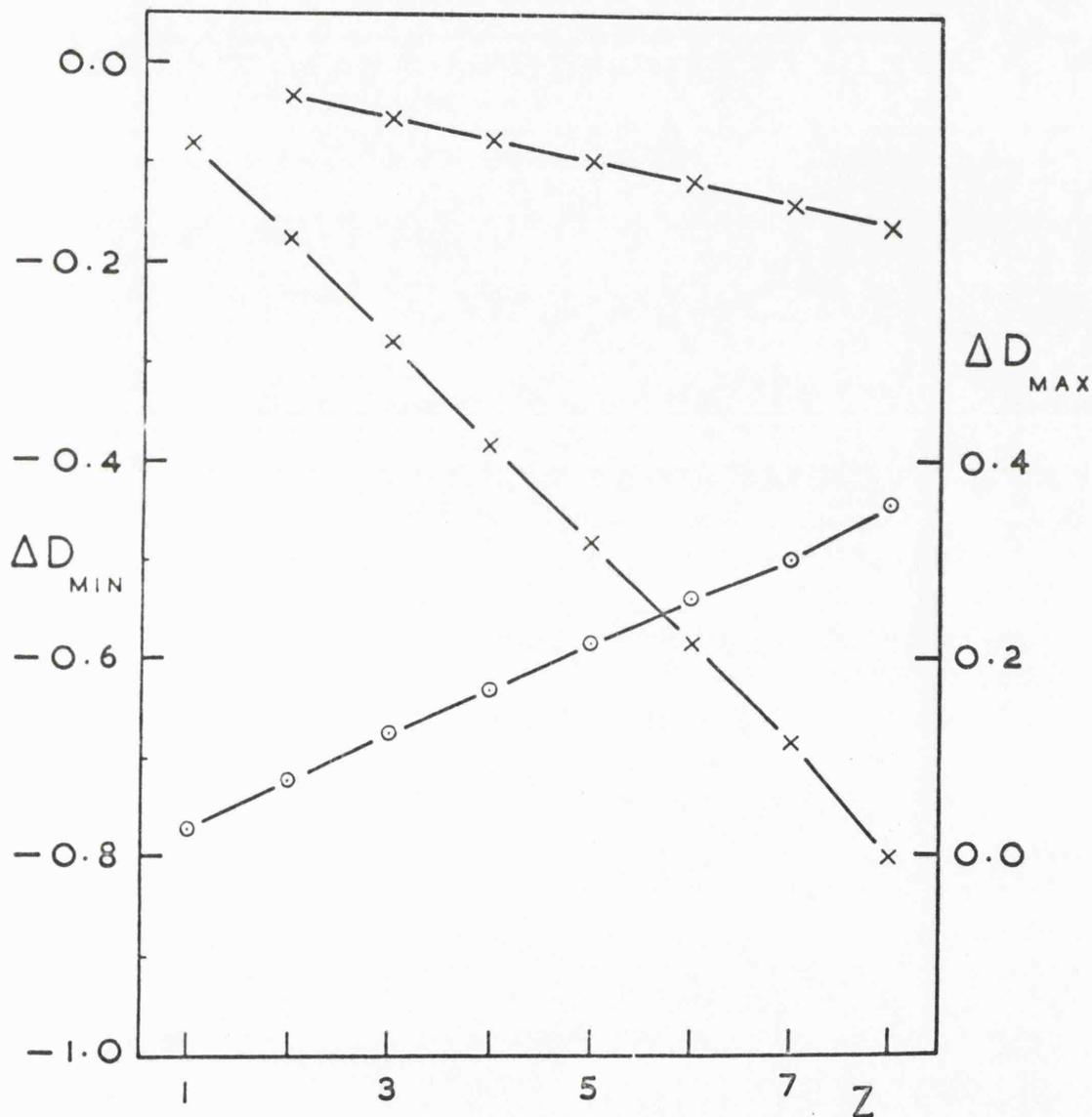
Fig. 2 . The two-particle density differences  $\Delta D(r_1, r_2)$  for  $\text{H}^-$ ,  $\text{He}$  and  $\text{Li}^+$ , plotted as a function of  $r_1 = r_2$ . The solid curves represent the functions of Weiss (I), the dashed curves those of Green et al (II) and the dots within circles those of Stuart and Matsen (III).



**Fig. 3** . The radial density distributions  $D(r)$  for  $\text{H}^-$ , He and  $\text{Li}^+$ . The solid curves represent the functions of Weiss (I), the dashes those of Green et al (II) and alternate long and short dashes those of Stuart and Matsen (III). Results from the Hartree-Fock functions are represented by crosses. The origins have been separated for clarity.



**Fig. 4** . The coherent X-ray scattering factor  $f_{\infty}(X)$  for  $H^-$ , He and  $Li^+$ , where  $X = (\sin \theta / 2) / \lambda$ . The solid curves represent the functions of Weiss (I) and the dashes those of Green et al (II). Results from the Hartree-Fock functions are represented by crosses. Also shown are the X-ray scattering factors from the corresponding one-electron systems.



**Fig. 5 .** Values of the minima  $\Delta D_{\text{MIN}}$  (—x—x—) and the maxima  $\Delta D_{\text{MAX}}$  (—o—o—) which occur in the  $\Delta D(r_1, r_2)$  surfaces, for various Z.

NATURAL EXPANSIONS FOR THE WEISS FUNCTIONS.

In the following pages are presented the natural expansions of the wave-functions of Weiss for  $H^-$  through to  $O^{6+}$ . Alongside each coefficient is the symmetry of the basis orbitals composing the corresponding natural orbital. Within each natural orbital the basis orbitals are ordered as follows:

1s	2s	1s'	2s'	3s'
2p	3p	2p'	3p'	3d
4d	5d	4f	5f	5g

NATURAL    EXPANSION    WEISS    H<sup>-</sup>

COEFFICIENTS:	1.	-0.97152	s
	2.	0.20768	s
	3.	0.11001	p
	4.	0.01775	d
	5.	0.01574	p
	6.	0.01411	s
	7.	0.00585	f
	8.	0.00511	d
	9.	0.00376	p
	10.	0.00330	s
	11.	0.00250	g
	12.	0.00205	f
	13.	0.00181	d
	14.	0.00161	p
	15.	0.00005	s

NATURAL    ORBITALS:

1.	0.52468	-0.05643	0.58226	-0.05171	0.11521
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
2.	-0.95546	0.04964	1.03708	0.17798	-0.34154
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.49676	0.27499	0.04388	0.23286	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
4.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.35107
	0.13438	0.56201	0.00000	0.00000	0.00000
5.	0.00000	0.00000	0.00000	0.00000	0.00000
	-2.21175	0.19278	1.07968	1.27509	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
6.	-2.17573	0.68233	-1.63147	3.13155	0.02988
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.07085	0.93253	0.00000
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	-1.17363
	-0.79726	1.93899	0.00000	0.00000	0.00000
9.	0.00000	0.00000	0.00000	0.00000	0.00000
	1.91058	-2.26249	-2.83402	2.55404	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
10.	6.47069	-2.76863	-3.88488	6.65113	-7.88476
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
11.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	1.00000
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	-3.16149	3.02165	0.00000
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	-5.87359
	11.63400	-6.39720	0.00000	0.00000	0.00000
14.	0.00000	0.00000	0.00000	0.00000	0.00000
	-19.86200	10.40200	0.97155	10.25800	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
15.	-8.31102	5.37324	1.63036	-0.09866	3.23647
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

NATURAL EXPANSION WEISS He

COEFFICIENTS:			
	1.	-0.99598	s
	2.	0.06191	p
	3.	0.06163	s
	4.	0.01265	d
	5.	0.01114	p
	6.	0.00790	s
	7.	0.00448	f
	8.	0.00390	d
	9.	0.00328	p
	10.	0.00192	s
	11.	0.00180	g
	12.	0.00160	f
	13.	0.00132	d
	14.	0.00087	p
	15.	0.00065	s

NATURAL ORBITALS:

1.	0.80993	0.03551	0.13058	0.04664	0.01759
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
2.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.67022	0.34367	-0.04042	0.03881	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
3.	-1.27631	-0.39473	0.81373	0.79650	0.22014
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
4.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.26932
	0.27368	0.49618	0.00000	0.00000	0.00000
5.	0.00000	0.00000	0.00000	0.00000	0.00000
	1.28594	-1.84345	-0.03997	0.63209	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
6.	-1.68995	-0.59918	-0.32041	-0.34839	2.92986
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

7.	0,00000	0,00000	0,00000	0,00000	0,00000
	0,00000	0,00000	0,00000	0,00000	0,00000
	0,00000	0,00000	0,11662	0,88869	0,00000
8.	0,00000	0,00000	0,00000	0,00000	0,00000
	0,00000	0,00000	0,00000	0,00000	-0,83024
	-1,47737	2,30624	0,00000	0,00000	0,00000
9.	0,00000	0,00000	0,00000	0,00000	0,00000
	9,77523	-6,02307	-2,31192	-2,82569	0,00000
	0,00000	0,00000	0,00000	0,00000	0,00000
10.	-17,83500	8,34930	3,19498	5,29376	3,58996
	0,00000	0,00000	0,00000	0,00000	0,00000
	0,00000	0,00000	0,00000	0,00000	0,00000
11.	0,00000	0,00000	0,00000	0,00000	0,00000
	0,00000	0,00000	0,00000	0,00000	0,00000
	0,00000	0,00000	0,00000	0,00000	1,00000
12.	0,00000	0,00000	0,00000	0,00000	0,00000
	0,00000	0,00000	0,00000	0,00000	0,00000
	0,00000	0,00000	-3,16013	3,03484	0,00000
13.	0,00000	0,00000	0,00000	0,00000	0,00000
	0,00000	0,00000	0,00000	0,00000	-5,93622
	11,56500	-6,27979	0,00000	0,00000	0,00000
14.	0,00000	0,00000	0,00000	0,00000	0,00000
	-12,39100	6,41397	-1,61742	8,51748	0,00000
	0,00000	0,00000	0,00000	0,00000	0,00000
15.	-23,28100	9,14122	9,54034	-4,53001	13,08400
	0,00000	0,00000	0,00000	0,00000	0,00000
	0,00000	0,00000	0,00000	0,00000	0,00000

NATURAL EXPANSION WEISS Li<sup>+</sup>

COEFFICIENTS:	1.	-0.99840	s
	2.	0.04149	p
	3.	0.03691	s
	4.	0.00903	d
	5.	0.00779	p
	6.	0.00521	s
	7.	0.00326	f
	8.	0.00280	d
	9.	0.00230	p
	10.	0.00131	s
	11.	0.00129	g
	12.	0.00115	f
	13.	0.00091	d
	14.	0.00055	p
	15.	0.00044	s

NATURAL ORBITALS:

1.	0.85231	0.04635	0.08948	0.03039	0.00873
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
2.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.58720	0.43516	-0.03432	0.02599	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
3.	-1.52435	-0.39537	0.94112	0.94246	0.22001
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
4.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.24772
	0.25771	0.53288	0.00000	0.00000	0.00000
5.	0.00000	0.00000	0.00000	0.00000	0.00000
	2.04759	-2.27589	-0.20443	0.40485	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
6.	-3.04964	-0.37629	0.13206	0.00129	3.44794
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.09363	0.91073	0.00000
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	-0.68819
	-1.76755	2.45105	0.00000	0.00000	0.00000
9.	0.00000	0.00000	0.00000	0.00000	0.00000
	10.19700	-6.15276	-2.22886	-3.23942	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
10.	24.90400	-10.61300	-5.89157	-7.16158	-4.59830
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
11.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	1.00000
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	-3.16089	3.02830	0.00000
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	-5.95532
	11.52400	-6.22169	0.00000	0.00000	0.00000
14.	0.00000	0.00000	0.00000	0.00000	0.00000
	-11.94500	6.14078	-1.71856	8.38308	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
15.	-33.79700	12.13700	13.56700	-2.29123	15.56500
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

NATURAL EXPANSION WEISS Be<sup>2+</sup>

COEFFICIENTS:	1.	-0.99916	s
	2.	0.03112	p
	3.	0.02637	s
	4.	0.00694	d
	5.	0.00594	p
	6.	0.00388	s
	7.	0.00254	f
	8.	0.00215	d
	9.	0.00175	p
	10.	0.00099	s
	11.	0.00098	g
	12.	0.00089	f
	13.	0.00068	d
	14.	0.00040	p
	15.	0.00034	s

NATURAL ORBITALS:

1.	0.87655	0.04803	0.06849	0.02271	0.00567
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
2.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.54125	0.48116	-0.02979	0.02280	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
3.	-1.69390	-0.37594	1.02271	1.02507	0.22211
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
4.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.23550
	0.21615	0.58658	0.00000	0.00000	0.00000
5.	0.00000	0.00000	0.00000	0.00000	0.00000
	2.38714	-2.46548	-0.27547	0.29832	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
6.	-4.03066	-0.18169	0.48210	0.25789	3.75130
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.08535	0.91867	0.00000
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	-0.57218
	-2.00620	2.56514	0.00000	0.00000	0.00000
9.	0.00000	0.00000	0.00000	0.00000	0.00000
	10.33500	-6.18426	-2.19050	-3.39814	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
10.	29.08100	-11.88300	-7.59910	-8.23956	-5.15691
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
11.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	1.00000
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	-3.16113	3.02590	0.00000
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	-5.96801
	11.48600	-6.17058	0.00000	0.00000	0.00000
14.	0.00000	0.00000	0.00000	0.00000	0.00000
	11.76400	-6.03135	1.75762	-8.32439	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
15.	-39.91700	13.77300	16.07000	-0.90479	16.83300
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

NATURAL EXPANSION WEISS B<sup>3+</sup>

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COEFFICIENTS:			
	1.	-0.99947	s
	2.	0.02489	p
	3.	0.02052	s
	4.	0.00564	d
	5.	0.00479	p
	6.	0.00309	s
	7.	0.00201	f
	8.	0.00174	d
	9.	0.00140	p
	10.	0.00081	s
	11.	0.00080	g
	12.	0.00065	f
	13.	0.00054	d
	14.	0.00031	p
	15.	0.00028	s

NATURAL ORBITALS:

1.	0.89907	0.04126	0.05500	0.01784	0.00397
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
2.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.51233	0.50894	-0.02702	0.02209	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
3.	-1.83900	-0.33784	1.08396	1.08138	0.22606
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
4.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.22928
	0.18973	0.61908	0.00000	0.00000	0.00000
5.	0.00000	0.00000	0.00000	0.00000	0.00000
	2.57885	-2.57163	-0.31526	0.23712	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
6.	-4.64279	-0.04913	0.70501	0.42085	3.91897
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	-0.07761	1.07332	0.00000
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	-0.50640
	-2.14061	2.62847	0.00000	0.00000	0.00000
9.	0.00000	0.00000	0.00000	0.00000	0.00000
	10.40800	-6.19906	-2.16740	-3.48645	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
10.	31.81500	-12.71800	-8.74233	-8.80278	-5.65085
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
11.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	1.00000
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	3.16133	-2.97456	0.00000
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	5.97428
	-11.46200	6.14079	0.00000	0.00000	0.00000
14.	0.00000	0.00000	0.00000	0.00000	0.00000
	11.66000	-5.96928	1.77947	-8.28981	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
15.	42.76100	-14.45700	-17.32400	0.26554	-17.39500
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

NATURAL    EXPANSION    WEISS    C<sup>4+</sup>

COEFFICIENTS:	1.	-0.99967	s
	2.	0.02072	p
	3.	0.01679	s
	4.	0.00476	d
	5.	0.00401	p
	6.	0.00256	s
	7.	0.00172	f
	8.	0.00147	d
	9.	0.00117	p
	10.	0.00067	g
	11.	0.00066	s
	12.	0.00056	f
	13.	0.00046	d
	14.	0.00026	p
	15.	0.00023	s

NATURAL ORBITALS:

1.	0.91382	0.03695	0.04593	0.01470	0.00300
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
2.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.49308	0.52741	-0.02487	0.02133	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
3.	-1.94039	-0.31137	1.12751	1.12004	0.22875
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
4.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.22908
	0.19312	0.61583	0.00000	0.00000	0.00000
5.	0.00000	0.00000	0.00000	0.00000	0.00000
	2.69859	-2.63710	-0.33890	0.19745	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
6.	-5.27828	0.11976	0.93100	0.57768	4.08073
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	-0.05843	1.05526	0.00000
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	-0.50094
	-2.15049	2.63445	0.00000	0.00000	0.00000
9.	0.00000	0.00000	0.00000	0.00000	0.00000
	10.44100	-6.20229	-2.15427	-3.53311	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
10.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	1.00000
11.	32.32900	-12.83100	-8.99112	-9.19569	-5.42042
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	-3.16174	2.98101	0.00000
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	-5.97477
	11.46100	-6.13859	0.00000	0.00000	0.00000
14.	0.00000	0.00000	0.00000	0.00000	0.00000
	11.60400	-5.93572	1.79107	-8.27109	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
15.	-45.75800	15.33000	18.49500	0.47078	17.94500
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

NATURAL EXPANSION WEISS N<sup>5+</sup>

COEFFICIENTS:	1.	-0.99978	s
	2.	0.01775	p
	3.	0.01422	s
	4.	0.00409	d
	5.	0.00346	p
	6.	0.00219	s
	7.	0.00150	f
	8.	0.00127	d
	9.	0.00101	p
	10.	0.00058	g
	11.	0.00057	s
	12.	0.00049	f
	13.	0.00039	d
	14.	0.00022	p
	15.	0.00020	s

NATURAL ORBITALS:

1.	0.92441	0.03390	0.03918	0.01257	0.00248
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
2.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.48038	0.53932	-0.02344	0.02114	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
3.	-1.99647	-0.29758	1.14789	1.13984	0.23767
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
4.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.22391
	0.17774	0.63609	0.00000	0.00000	0.00000
5.	0.00000	0.00000	0.00000	0.00000	0.00000
	2.76614	-2.67337	-0.35115	0.17396	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
6.	-5.32400	0.10728	0.96133	0.58346	4.10647
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	-0.03220	1.03050	0.00000
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	-0.46852
	-2.21763	2.66450	0.00000	0.00000	0.00000
9.	0.00000	0.00000	0.00000	0.00000	0.00000
	10.46800	-6.20852	-2.14556	-3.56486	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
10.	33.62500	-13.23100	-9.52659	-9.35991	-5.77359
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
11.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	1.00000
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	-3.16211	2.98966	0.00000
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	5.97746
	-11.44800	6.12334	0.00000	0.00000	0.00000
14.	0.00000	0.00000	0.00000	0.00000	0.00000
	-11.56400	5.91174	-1.79916	8.25791	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
15.	-46.17300	15.36800	18.74600	0.54568	18.02900
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

NATURAL EXPANSION WEISS  $O^{6+}$

COEFFICIENTS:			
	1.	-0.99984	s
	2.	0.01554	p
	3.	0.01233	s
	4.	0.00361	d
	5.	0.00303	p
	6.	0.00191	s
	7.	0.00131	f
	8.	0.00112	d
	9.	0.00088	p
	10.	0.00050	s
	11.	0.00049	g
	12.	0.00044	f
	13.	0.00034	d
	14.	0.00019	p
	15.	0.00017	s

NATURAL ORBITALS:

1.	0.92941	0.03423	0.03481	0.01099	0.00207
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
2.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.47005	0.54825	-0.02187	0.02159	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
3.	-2.05613	-0.28667	1.18125	1.16731	0.22950
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
4.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.22526
	0.18387	0.62866	0.00000	0.00000	0.00000
5.	0.00000	0.00000	0.00000	0.00000	0.00000
	2.83464	-2.71173	-0.36499	0.15110	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
6.	-5.98037	0.27953	1.19573	0.76439	4.25428
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	-0.03851	1.03646	0.00000
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	-0.46935
	-2.21435	2.66479	0.00000	0.00000	0.00000
9.	0.00000	0.00000	0.00000	0.00000	0.00000
	10.48500	-6.20893	-2.13780	-3.59088	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
10.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	1.00000
11.	34.07200	-13.31800	-9.76154	-9.74885	-5.50880
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	3.16205	-2.98760	0.00000
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	5.97734
	-11.44800	6.12399	0.00000	0.00000	0.00000
14.	0.00000	0.00000	0.00000	0.00000	0.00000
	11.53200	-5.89296	1.80565	-8.24708	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
15.	49.39500	-16.29400	-20.02300	-1.34349	-18.60300
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000

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**PART II**

CHAPTER 1.

INTRODUCTION.

The helium hydride molecular ion  $\text{HeH}^+$  is the simplest two-electron heteronuclear diatomic system and as such plays a role analogous to that of the hydrogen molecule in homonuclear systems. The generally accepted equilibrium bond length is only slightly greater than that of  $\text{H}_2$ , and although the binding energy is only about 40% of that of  $\text{H}_2$ , it nevertheless forms quite a strong bond.  $\text{HeH}^+$  is a one-centre system both at  $R=0$ , when we have the united atom  $\text{Li}^+$ , and at  $R=\infty$ , when we have the helium atom. Thus it is the simplest molecule of the form  $\text{MH}^+$  (where M is an element whose ionization potential is greater than that of the hydrogen atom), which in the ground state dissociates according to  $\text{MH}^+ \rightarrow \text{M} + \text{H}^+$ .

It was first observed around 1933<sup>(1)</sup>, in mass spectrometers, along with  $\text{NeH}^+$  and  $\text{ArH}^+$ . Because these rare-gas hydride ions have only a short lifetime and are formed in low concentrations, experimental measurements of their properties are very difficult. This in itself admits a need for accurate theoretical treatments of the systems.

Besides this, however,  $\text{HeH}^+$  is particularly important because  $\text{He}^3\text{H}^+$  is the daughter ion which results when tritium in the tritium hydride molecule undergoes  $\beta$ -decay. Investigation of this decay

process has been undertaken theoretically, and it has been the sole reason for the production of at least one extremely accurate wave-function for the ground state of  $\text{HeH}^+$ .

Some knowledge of the molecular states of  $\text{HeH}^+$  is also desirable because it is thought to form an important constituent of some stellar systems. The existence of a flux deficiency in the spectra of certain stars was thought to be due to absorption by  $\text{HeH}^+$  in the surface layers. WERNER <sup>( 2 )</sup> used some theoretical treatments to investigate this and discounted the explanation that the flux deficiency was due to transitions from the ground to the first excited state. He did not entirely rule out, however, the possible cause as being transitions between higher excited states.

The points outlined above are ample explanation for the large number of theoretical calculations which have been performed on  $\text{HeH}^+$  since the early years of quantum mechanics. These calculations have been extremely varied in type and accuracy. There follows a brief review of the most important of these, the majority of which are concerned solely with the ground state.

The theoretical treatment of  $\text{HeH}^+$  began in 1933 when GLOCKLER and FULLER <sup>( 3 )</sup> applied the techniques of wave mechanics to the system. They had predicted the existence of such an ion earlier. Then, when BAINBRIDGE <sup>( 1 )</sup> made his experimental observation of the system, they sought to put this on a theoretical footing. They made two attempts

at a quantum-mechanical solution. The first was based on the interaction of an excited helium atom and a proton, and the system was found to be repulsive for all internuclear separations. The second used the interaction of a helium ion with a hydrogen atom. On neglecting one integral, because it would have taken too long to evaluate, they obtained a binding energy of 8.1 e.V., and thought that they had in fact obtained a satisfactory theoretical solution. The neglected integral was the unsymmetric Sugiura integral, whose inclusion reduces the binding energy from 8.1 e.V. to 3.6 e.V. We now know that the ground state of  $\text{HeH}^+$  connects energetically with a helium atom and a proton, so that Glockler and Fuller were optimistic in their conclusion. Thus the theoretical treatment of  $\text{HeH}^+$  did not begin in a very auspicious manner.

In 1938 COULSON and DUNCANSON<sup>(4)</sup> made a comparative study on  $\text{HeH}^+$  using various different types of wave-function. Among these were a molecular orbital and a valence bond calculation, of which the former was found to be better. Another of their wave-functions was of the James-Coolidge type, and in 1940 TOH<sup>(5)</sup> extended this work with a ten- and a twelve- term James-Coolidge function. With the work of EVETT<sup>(6)</sup> in 1956 we have the first really large calculation on  $\text{HeH}^+$ . Evett chose to extend Toh's work with a twenty- and a twenty-three-term James-Coolidge function. In doing so he was able to check Toh's results, whereby he found some numerical errors in the latter's work. Up to this point, calculations on  $\text{HeH}^+$  had predicted varied

results for both the binding energy and the equilibrium bond length. Evett's results were 1.90 e.V. <sup>(a)</sup> and 1.432 a.u. respectively, which are not very far from today's generally accepted values.

With the work of ANEX <sup>(7)</sup> in 1963 we have another large-scale calculation, a product of the age of high-speed computers. Anex maximized the then available computing facilities in producing a thirty-five-term configuration interaction wave-function with one-electron basis functions in elliptical co-ordinates. His values for binding energy and equilibrium bond length of 1.931 e.V. and 1.446 a.u. were extremely close to those of Evett. Anex produced wave-functions at four different bond lengths. He also produced a SCF wave-function, which, in combination with the CI, gave information about the correlation energy in the system. This was estimated at 0.045 a.u., and was found to be more or less constant with bond length.

In 1964 STUART and MATSEN <sup>(8)</sup> published the first extensive one-centre calculation on the ground state of HeH<sup>+</sup>. The total wave-function consisted of a thirty-term superposition of configurations using a basis of Slater-type orbitals, up to 101. The calculation was done at twelve different values of the bond length, ranging from 0.1 a.u. to 5.0 a.u.. In addition Stuart and Matsen presented limited CI functions for Li<sup>+</sup> and He. These were constructed from ten configurations and conformed to the accuracy attained in the molecular

(a) 1 a.u. = 27.2097 e.V..

calculation. The values of 1.852 e.V. and 1.464 a.u. for binding energy and equilibrium separation fitted in well with the results of Evett and of Anex, whilst the total energy (at 1.4 a.u.) of -2.9691 a.u. ranked third in excellence up to this point behind -2.9742 a.u. of Anex and -2.9730 a.u. of Evett.

The calculation of PEYERIMHOFF<sup>(9)</sup> in 1965 yielded the first really extensive LCAO SCF function. BHATTACHARYA<sup>(10)</sup> had produced a simple LCAO but his results were optimistic because of incomplete optimization of non-linear parameters. Peyerimhoff's was an extensive study for a range of bond lengths, in which she used a 4x2 (four orbitals centred on He, two on H) basis and a 7x5 basis to make up the LCAO molecular orbital. The basis orbitals were STO's. In each case, results were presented for orbital exponents optimized both at 1.455 a.u. (the equilibrium bond length) and at each R value, the range of bond lengths being from 1.0 a.u. to 4.5 a.u.. Results for binding energy and minimum total energy were 1.943 e.V. and -2.93313 a.u. respectively.

Peyerimhoff was the first worker to present a wide range of physical properties. Among these were spectroscopic constants and the variation of the centre of charge with bond length. Also presented were potential curves, curves of the variation of the forces on the two nuclei with bond length, and density contours of the total electronic charge in the molecule.

WOLNIEWICZ,<sup>(11)</sup> in 1965, was prompted into making his calculation

by the wish to test a surprising experimental result. SNELL,  
(12)  
PLEASONTON and LEMING, working on the  $\beta$ -decay of tritium in  
tritium hydride, had found that the molecule remained bound after  
decay in 93.2% of cases. Wolniewicz attempted to test this unexpected  
result but found that theoretical treatments of both the parent, HT,  
and the daughter, HeH<sup>+</sup> (or more exactly He<sup>3</sup>H<sup>+</sup>), were unreliable. To  
remedy this situation he produced a wave-function which has so far  
given the lowest energy for HeH<sup>+</sup>, -2.97866 a.u. at the equilibrium  
bond length of 1.4632 a.u.. Basing his work on that of Evett, he  
extended this from a twenty-three-term to a sixty-four-term James-  
Coolidge function. For the binding energy he obtained 2.039 e.V. and  
for the total energy at R=1.4 a.u. he obtained -2.97797 a.u.. With  
this extremely accurate and elaborate function he tested theoretically  
the experimental result of Snell, Pleasonton and Leming. He concluded  
that the theoretical dissociation rate in the decay process was  
something larger than 17.8%, much greater than the 6.8% predicted by  
experiment. Wolniewicz believed his function to be "rather accurate",  
due to its high flexibility.

Of the later work on the ground state, that of HOYLAND<sup>(13)</sup> is  
worthy of note in that he used non-integral elliptical orbitals in a  
part-SCF, part-CI study. The SCF results were compared with those of  
Peyerimhoff, and indicated a very similar result with fewer terms.  
Comparison of the CI work with that of Anex indicated that non-  
integral n-values brought faster convergence than a truncated

natural expansion.

The work of HARRIS<sup>(14)</sup> gave the same result that Anex found, that the correlation energy was almost independent of internuclear separation. This paper is one of the last to concentrate solely on the ground state, and later work looks at some of the lower and higher excited states. For instance, MICHELS<sup>(15)</sup>, in 1966, examined fourteen excited states of  $\Sigma$  and  $\Pi$  symmetry. Among the most recent calculations, that by BARTOLOTTI and GOODISMAN<sup>(16)</sup> is interesting in that it invoked the bare-nucleus perturbation theory, where the full interelectronic interaction is taken as a perturbation. The equilibrium bond length obtained was 1.448 a.u., very close to the accepted value, whilst the energy at  $R=1.4$  a.u. was -2.97478 a.u., to be compared with the values of -2.97797 a.u. by Wolniewicz and -2.9742 a.u. by Anex.

Of this extensive list of calculations on  $\text{HeH}^+$ , one in particular seems to stand out as being worthy of further investigation. This is the one-centre calculation of Stuart and Matsen. No other wave-function is presented over such a wide range of bond lengths. In conjunction with this, the presentation of the wave-functions for the He atom and the  $\text{Li}^+$  ion offers a perfect opportunity to test how the wave-function predicts the formation of the molecule. Using a popular method, that of density difference maps, this has been done. By means also of physical properties calculated at the

different bond lengths, extra information has been obtained as to the effect the proton has on the density, as predicted by this approximation, as it changes its position relative to the He nucleus. The results from these investigations are presented and discussed in the next chapter.

Subsequent to his original calculation, ANEX together with SHULL<sup>(17)</sup> analysed the configuration interaction wave-function into the form of the natural expansion. They analysed both an all-sigma-basis wave-function and the total wave-function in this way and demonstrated the rapid convergence of the natural expansion from the point of view of the energy. In addition they attempted to rationalize the trends which appeared in the variation of the natural expansion coefficients with bond length. We have analysed the Stuart and Matsen wave-functions into natural orbitals over the entire range of bond length, and in Chapter 3 the results are discussed in comparison with those of Anex and Shull. The Stuart and Matsen wave-functions were composed of Slater-type orbitals centred on the helium nucleus, whilst those of Anex were built up from essentially two-centre functions. Here, then, is a splendid starting point from which to test the natural expansion in reducing the influence of the arbitrary nature of the choice of the basis set. Results from this comparison are also presented in Chapter 3.

CHAPTER 2.

MOLECULAR FORMATION.

A popular and useful method of studying the changes which occur when a molecule is formed is through the use of density contours and density difference maps. The work of KERN and KARPLUS<sup>(18)</sup>, BADER and HENNEKER<sup>(19)</sup>, and BADER, HENNEKER and CADE<sup>(20)</sup>, is especially noteworthy in this connection. We begin this study of Stuart and Matsen's one-centre wave-function for  $\text{HeH}^+$  by presenting maps of the one-electron density of the molecule-ion minus that of an isolated helium atom. By drawing these maps for a wide range of bond lengths, it may clearly be seen what effect the proton has on the density in  $\text{HeH}^+$ , as predicted by this calculation, as its proximity to the He nucleus increases.

These one-electron density difference maps are presented in Fig. 1 (a) to (f). In Fig. 1 (a), it may be seen that the proton, at 5.0 a.u. from the He nucleus, is having only a small effect on the electron density. There has been a transfer of charge from the side of the He nucleus remote from the proton into the region between the nuclei, but the amount of this charge-transfer is slight. Though it forms a build-up between the nuclei, this again is only slight and it seems to be influenced more by the He nucleus than by the proton, since the position of the maximum is at only about

0.4 a.u. from the He nucleus. By the time the proton has moved in to be 3.0 a.u. from the He nucleus, Fig. 1 (b), it is having a far greater effect. The amount of charge transferred to the region between the nuclei is considerably larger, and the density as a whole has become more diffuse. The He nucleus is firmly embedded in the region of negative density difference, whereas previously the zero contour was only just to the right of this nucleus. The zero contour has begun to be bent round towards the proton. The maximum of the pile-up of charge has now moved out to 1.0 a.u. from the He nucleus. The same trends continue, as may be seen from Fig. 1 (c), when the proton is at 2.0 a.u. from the He nucleus. The pile-up of charge has continued and is now at a maximum at 1.10 a.u.. The zero contour has bent round more and is a little further still to the right of the He nucleus.

The effect of the proton has thus far shown a gradual but definite increase. The next diagram, Fig. 1 (d), shows the proton at a distance of 1.4 a.u. from the He nucleus, very close to the theoretical bond length of  $\text{HeH}^+$ ; the effect of the proton has now become very strong. The charge build-up between the nuclei, with its maximum located at 0.9 a.u., is considerable. The zero contour has been bent round more and more towards the proton, and the density has become correspondingly more contracted. A charge build-up of this kind is of course to be expected at around this bond length. It is worth noting that the He nucleus is now only just, but

nevertheless unmistakably, in the region of negative density difference, showing that the density on the heavy nucleus in the molecule-ion at the equilibrium bond length is less than that in the isolated helium atom. The negative contours are seen to be being gradually drawn round with the zero contour. Moving on to Fig. 1 (e), the proton is now 1.0 a.u. from the He nucleus, considerably less than the equilibrium bond length for  $\text{HeH}^+$ . The approach of the proton towards the He nucleus appears to have forced the zero contour in front of it, because the He nucleus now resides firmly in the region of positive density difference. The maximum of charge is between the nuclei but proportionately closer to the proton than has been the case so far. The position of the maximum is approximately 0.75 a.u. from the He nucleus. The zero contour has swung round markedly, enclosing the positive contours and drawing the negative contours around with it. By the time the proton has moved in to 0.1 a.u. from the He nucleus, see Fig. 1 (f), the density of the ion has become very nearly spherically symmetrical. The positive contours are now completely enveloped within the zero contour and are almost semi-circular. Their slight variation from exact semi-circular shape, plus the behaviour of the negative contours in this case, indicate a very slight polarization of the charge to the proton side of the He nucleus.

As remarked by Bader, Henneker and Cade, "as important as the amount of charge is the exact disposition of charge in the molecule".

This point is very well brought in these diagrams. When the internuclear distance is 5.0 a.u. there is already a pile-up of charge between the nuclei, but this is so slight and so far from the proton that one could hardly expect a respectable bond. As the proton moves in, however, the situation rapidly improves. The amount of charge in the "bonding region" increases and moves proportionately nearer to the proton. In doing so it serves to exert a greater attractive force on the proton, and at the same time to screen more effectively the repulsion between the two nuclei. When the distance between the nuclei is 1.4 a.u. we evidently have the optimum conditions, with a good pile-up of charge between the He nucleus and the proton, and the position of the maximum dividing the He - H distance very closely in the ratio 2:1. Inside 1.4 a.u. the build-up has apparently become too large and too close to the proton to give the best conditions for stability in the system.

Though the density difference maps just discussed show most clearly the behaviour of the electronic charge during molecular formation, this may also be illustrated by the graphs of the one-particle radial density distribution  $D(r)$ . (See Part I, Equ. 3(4).) In Fig. 2 these are plotted for  $\text{Li}^+$ , He and some intermediate bond lengths for  $\text{HeH}^+$ . The He atom  $D(r)$  could not be distinguished on this scale from the  $\text{HeH}^+$   $R=5.0$   $D(r)$ , so the latter is not shown. This is also the case for  $R=3.0$  and  $R=4.0$ , although close inspection of the

data shows that the proton is beginning to have an effect in making the corresponding  $D(r)$  spread slightly. This effect is most marked for  $R=2.0$  a.u., as shown, after which the proton begins to pull charge in with it and makes the  $D(r)$  contract. The graphs show that for smaller bond lengths the  $D(r)$  curves gradually begin to resemble that for  $\text{Li}^+$ , until for  $R=0.1$  the respective  $D(r)$  curves are indistinguishable. These results indicate that the proton, from having very little influence at large values of  $R$ , so that the density is little different from that for an isolated He atom, has a gradually increasing effect as it is moved in. This is what one would expect from such a system, which in the ground state dissociates into a normal helium atom and a proton. Peyerimhoff and Anex found a similar state of affairs in calculating the centre of negative charge. Their results indicated that if the proton were within a distance from the He nucleus smaller than the equilibrium bond length then the charge cloud tended to follow it, but that if this distance increased from  $R_e$  the charge cloud moved steadily back towards the unperturbed position which it would have in the He atom.

The graphical indistinguishability of the  $D(r)$  curves is a disadvantage which may be overcome if we look instead at the values of  $\langle r^n \rangle$ , where  $-2 \leq n \leq 4$ . (See Part I, Equ. 3(5).) In Fig. 3 these are plotted as a function of internuclear distance, and they indicate the same trends as did the  $D(r)$  curves but with greater clarity. For  $n=-2$  and  $-1$  the curves each have a minimum at  $R$  approx-

imately equal to 1.8 a.u.. The curves for the positive values of  $n$  each have a maximum at around  $R=2.5$  a.u.. For  $n=1$  and 2 the maximum is barely perceptible but it becomes clearer for  $n=3$  and very pronounced for  $n=4$ . This indicates that in the middle regions of the system the density is not greatly affected by the proton, but that in the outer regions the density is most distended at values of  $R$  around 2.5 a.u.. These conclusions underline those from the  $D(r)$  curves and concur with those from the centre of charge calculations of Peyerimhoff and of Anex.

CHAPTER 3.

ELECTRON CORRELATION AND NSO ANALYSIS.

In the first section of this chapter we examine by means of density differences and expectation values the electron correlation present in the  $\text{HeH}^+$  wave-functions of Stuart and Matsen. Later, the results of a natural spin orbital analysis of these functions are presented and compared with those from a similar analysis on  $\text{HeH}^+$  wave-functions by Anex and Shull.<sup>(17)</sup>

The density difference map in Fig. 4 was obtained by subtracting the one-particle density as predicted by the natural expansion truncated to the first configuration from that for the total wave-function for  $\text{HeH}^+$ , at a common bond length of 1.4 a.u.. This is intended to give a representation of the effect of correlation in the molecule, bearing in mind that the closeness of  $\chi_1$  to the SCF orbital leads to a good approximation to the uncorrelated function. Fig. 4 shows some striking points. In the region between the nuclei correlation evidently has the effect of removing charge, whilst piling charge up on the nuclei themselves. The neatly localized form of the increase of charge on the proton is rather remarkable in view of the one-centre nature of the approximation under consideration. Also very interesting is the increase of

charge which correlation causes at right-angles to the bond axis, on and around a line through the helium nucleus.

From the increase in charge on the nuclei, and the simultaneous decrease between them, it might be conjectured that the equilibrium bond length predicted by a correlated treatment should be slightly greater than that from a non-correlated approach. Thus, the lower charge between the nuclei in a correlated density may cause the nuclear repulsion to be relatively more effective and hence provide a corresponding relaxation of the bond length. The equilibrium bond length  $R_e$  as predicted by Peyerimhoff's SCF function is 1.455 a.u.. The correlated functions of Wolniewicz and of Stuart and Matsen predict 1.4632 a.u. and 1.464 a.u., respectively, and so are in line with the above hypothesis. The values of 1.446 a.u. and 1.432 a.u., however, due to Anex and Evett, respectively, are contrary to it. Actual figures therefore leave the question an open one.

The discussion above is unsatisfactory in that the figures given correspond to different approximations. It would be better if a comparison could be made within the same model, between a correlated and an uncorrelated function. Here again the Stuart and Matsen functions would be most useful because they are presented at several bond lengths very close to the equilibrium value. Potential curves could be drawn corresponding to the total wave-functions and to the natural expansions truncated to the first configuration. From each

of these the equilibrium internuclear separation could be estimated, and the question as to which is larger might be resolved in a more rigid manner than the one used above.

The density differences along the internuclear axis in  $\text{HeH}^{\dagger}$  for a selection of bond lengths are plotted in Fig. 5. Here again, the density from the first NSO configuration has been subtracted from that for the total function at the same bond length. In general these curves have the features noticed in the density difference map, Fig. 4. In each case there is a pronounced negative minimum between the nuclei, accompanied by an increase of charge at or slightly behind the nuclei. Only for  $R=1.0$  a.u. is the density at the He nucleus from the correlated function less than that from the uncorrelated function. Inspection of data shows that a pile-up of charge exists in the outer regions on a line perpendicular to the internuclear axis through the helium nucleus for all the  $R$ -values presented in Fig. 5, just as was noticed for  $R=1.4$  a.u. in Fig. 4. The height of this maximum is in general only a very small fraction of that at the He nucleus itself and is therefore not easily shown graphically. However, it seems to be a feature common to all our difference functions.

In Table I we present values of  $\langle r^n \rangle$  (see Part I, Equ. 3(5)), relative to the He nucleus, calculated for different bond lengths. These are given as a function of the degree of truncation of the natural expansions, and are therefore analogous to those in Part I,

Table V. The symmetry of the basis orbitals making up each natural orbital may be ascertained from the tables of natural expansions at the end of Part II. The values of  $\langle r^n \rangle$  soon converge to the values from the total functions, with a maximum of six terms being required for convergence. We observe the general trend that in the inner and outer regions of the system, natural orbitals composed of  $\sigma$ -type orbitals expand  $D(r)$ , whilst those composed of  $\pi$ -,  $\delta$ - type orbitals usually contract it. This tendency is parallel to that noticed for the atoms in Part I, where radial configurations spread the density and angular configurations caused a contraction. Finally, we note in passing that for  $\langle r \rangle$ , which emphasizes the middle regions of the molecule, there is a steady convergence to the total value, regardless of the symmetry-type of the basis orbitals composing the added natural orbitals.

In Fig. 6 are diagrams representing the variation of  $\langle \cos \gamma_{12} \rangle$  (see Part I, Chapter 3) with internuclear distance  $R$ . On the right-hand vertical axis we give values of  $\gamma_{12}$  corresponding to the  $\langle \cos \gamma_{12} \rangle$  values given on the left-hand vertical axis. The upper graph, A, was calculated using the wave-function truncated to the first natural orbital configuration; the lower graph, B, corresponds to the total wave-function. Graph A shows a tendency towards  $\langle \cos \gamma_{12} \rangle = 0$  ( $\gamma_{12} = 90^\circ$ ) at  $R=0$  ( $\text{Li}^+$ ) and at  $R=\infty$  ( $\text{He}$ ). Considering that the wave-function is uncorrelated, this is an expected trend. For the united and separated atoms,  $\langle \cos \gamma_{12} \rangle$  should be exactly zero

for a wave-function which does not include correlation. This was found to be the case, see Part I. Thus, Curve A shows the expected behaviour at the ends of the range of  $R$ . The question arises, what happens to our convenient value of  $\gamma_{12} = 90^\circ$  for an uncorrelated wave-function when we move from an atom to a molecule? Here, we cannot expect the same argument to hold, since the extra positive charge, in our case a proton, causes polarization of the originally spherical charge-cloud. Thus, although we cannot expect a value of  $\gamma_{12}$  equal to  $90^\circ$ , we can expect a value fairly near to  $90^\circ$ , simply because it has this value at both ends of the range of internuclear separation. Graph A shows clearly that the value of  $\langle \cos \gamma_{12} \rangle$  in the molecule is at all times greater than that in the atoms. It has a minimum value at around  $R=0.9$  a.u. corresponding to  $\gamma_{12} = 87.65^\circ$ , so that from the point of view of  $\langle \cos \gamma_{12} \rangle$ , the uncorrelated system is least atom-like at this bond length. Thus, this graph shows that in the molecule the electrons are, on average, closer together than they were in the united and the separated atoms.

Graph B, although of the same general shape as Graph A, is considerably displaced towards smaller  $\langle \cos \gamma_{12} \rangle$  values, i.e. towards correspondingly larger  $\gamma_{12}$  values. The values of  $\langle \cos \gamma_{12} \rangle$  for  $\text{Li}^+$  and He from the Stuart and Matsen functions are also marked in Fig. 6. The ends of Graph B do not seem to approach these atomic values. In attempting to rationalize this, it is instructive to revert to Tables I A and VI A of Part I. In Table I A, it may be seen

that for He, the function of Weiss predicts 98.8% of the correlation energy whereas the Stuart and Matsen function predicts 94.8%. Similarly, for  $\text{Li}^+$ , the Weiss function gives 98.4% of the correlation energy and the Stuart and Matsen function 93.6%. From Table VI A it is seen that the values of  $\langle \cos \gamma_{12} \rangle$  for He are -0.06431 and -0.03768, and for  $\text{Li}^+$  they are -0.04367 and -0.02545, for the Weiss and the Stuart and Matsen functions respectively. Thus, although the difference in the predicted percentage correlation energies is not very large, the resulting values of  $\langle \cos \gamma_{12} \rangle$  are vastly different. The Stuart and Matsen values are in fact only about 60% of the Weiss values. The function  $\langle \cos \gamma_{12} \rangle$  thus appears to be a very sensitive gauge of the amount of correlation predicted by a particular wave-function, for atomic systems.

Turning to  $\text{HeH}^+$ , it is possible to calculate a rough value for the percentage correlation energy at a particular bond length. For convenience, we may follow Anex and consider that the correlation energy is practically constant with bond length at a value of about 0.045 a.u.. If we take Peyerimhoff's energies as "uncorrelated" we may calculate percentage correlation energies for the Stuart and Matsen functions according to:

$$\% \text{ correlation} = 100 \times [E(\text{Stuart \& Matsen}) - E(\text{Peyerimhoff})]/0.045 .$$

Using this expression, % correlation = 77 for  $R=1.0$  a.u., 80 for

$R=1.4$  a.u., 85 for  $R=2.0$  a.u., and 88 for  $R=4.0$  a.u.. Hence, throughout the molecule the Stuart and Matsen wave-functions at no time predict more than 90% of the correlation energy. This could explain why Graph B does not tend to the atomic values. The single-centre configuration interaction wave-function has two things demanded of it. It has simultaneously to predict molecular formation and put some electron correlation into the molecule. The behaviour of Graph B indicates that the approximation is falling down on this latter point. This is why it seems to be displaced bodily upwards, away from the correlated atomic values.

The position of Graph B relative to the uncorrelated curve, Graph A, is interesting. It is not the absolute values of  $\langle \cos \gamma_{12} \rangle$  but the values relative to Graph A which are important here. Fig. 4 and the curves of Fig. 5 showed that correlation tended to move large quantities of charge away from the region between the nuclei. The displacement of charge could result in the electrons being spread out, and on average being further away from each other than in the uncorrelated case. Graph B bears out this argument.

One of the claims for the natural expansion is that it reduces the influence of the arbitrary nature of the choice of basis set. In other words, wave-functions built up from quite different basis orbitals will have very similar NSO coefficients when put into the form of the natural expansion. This property was extensively

investigated by SHULL<sup>(21)</sup>, who analysed a very large number of hydrogen molecule ground state wave-functions in terms of natural orbitals. His analysis showed a very great similarity between all the functions, with the natural expansion coefficients  $c_l$  being relatively independent of the choice of basis functions. This close correspondence increased if the bases approached completeness.

This valuable property of the natural expansion has found a useful application in analysing the Stuart and Matsen wave-functions. The original configuration interaction functions contained thirty configurations, made up from twenty-six single-centre basis orbitals (STO's). Since the parameters were optimized at each of the twelve bond lengths, the result was effectively a different basis set at each R-value. This makes meaningful comparison between the twelve functions almost impossible; hence the need for an analysis which would somehow reduce the disparity between the functions.

It was mentioned earlier that Anex and Shull performed an NSO analysis on Anex's CI functions. These original functions were composed of an essentially two-centre basis. Anex and Shull analysed in terms of the natural expansion both a twenty-eight-term function, made up from seven  $\sigma$  basis orbitals, and a thirty-five-term function, made up from six  $\sigma$ , three  $\pi$  and two  $\delta$  basis orbitals. Thus, in the former case the natural expansion had seven configurations and in the latter case eleven. The original CI functions were produced by optimization of non-linear parameters at four bond lengths, and are

therefore subject to the same limitation as those of Stuart and Matsen - meaningful comparison between them is almost impossible. Anex and Shull performed the NSO analysis to reduce this disadvantage.

We have analysed the Stuart and Matsen functions in terms of natural orbitals and have calculated various quantities at different bond lengths. In addition, we have taken the opportunity of comparing these natural expansions with the corresponding Anex and Shull results. Since the original functions were built up in entirely different ways, the natural expansion gives us a method of drawing parallels between two calculations which are, superficially at least, quite different.

The results of the NSO analysis of the Stuart and Matsen functions are presented at the end of Part II, together with with the symmetry of the basis functions composing each natural orbital. Since there were twenty-six basis functions originally, one would have expected there to be twenty-six natural orbital coefficients. In fact thirteen of these were found to be effectively zero.

The curves in Fig. 7 show the variation of the first two natural orbital coefficients  $c_1$  (Graph A) and  $c_2$  (Graph B) with  $R$  for the Stuart and Matsen  $\text{HeH}^+$  functions. The atomic values are also indicated. The crosses represent the results of Anex and Shull. Both Graph A and Graph B have turning points around  $R=1.9$  a.u.. The Anex and Shull results indicate the same general trend and are very close to the Stuart and Matsen values. Whereas for  $c_1$  the Anex and

Shull results are usually higher, for  $c_2$  they lie below the Stuart and Matsen curve. In each case, A and B, the ends of the curves lie very close to the atomic values. In the case of He in particular, each curve approaches the atomic value asymptotically.

Further evidence of the closeness of the Stuart and Matsen and the Anex and Shull results is given in Table II. The internuclear distances  $R=1.0$  a.u. and  $R=1.4$  a.u. are the only two common to both calculations. Comparison of the two sets of results shows a very close correspondence between the magnitudes of the coefficients down at least as far as the fifth. Beyond this the agreement is not as good. This is understandable, because in each case the sum of the squares of the numbers has to equal unity. In the case of the Stuart and Matsen values this has to be "spread" over two more coefficients. The effect of this is that in general the Stuart and Matsen values are lower than the corresponding Anex and Shull values, with the disparity becoming more noticeable for the smaller coefficients. Considering the vastly different natures of the original approximations, the extent to which the natural expansion coefficients agree is remarkable. The symmetries of the basis orbitals composing the natural orbitals are also seen to agree precisely, except for the very last of all.

It seems appropriate at this point to make some comments on the signs of the natural expansion coefficients. Table II shows that there are disparities over signs between the Stuart and Matsen and

the Anex and Shull results, even though the magnitudes of the corresponding numbers are so close. The two-electron CI wave-function  $\psi$  is expressible as a real quadratic form (see Appendix):

$$\psi = \underline{\psi} \underline{C} \underline{\psi}^\dagger$$

where  $\underline{\psi}$  is a row vector of basis orbitals and  $\underline{C}$  is the matrix of the coefficients. By means of the transformation  $\underline{\chi} = \underline{\psi} \underline{A}$  this may be reduced to

$$\psi = \underline{\chi} \underline{c} \underline{\chi}^\dagger$$

which is a sum of squares if  $\underline{c}$  is diagonal. This is what has been done by throwing  $\psi$  into the form of the natural expansion. The number of terms in the diagonal form of  $\psi$  depends on  $\underline{C}$ . There are  $r$  terms if the rank of  $\underline{C}$  is  $r$ . Further, we may define the index  $p$  of the quadratic form as the number of the  $r$  terms which are positive and the signature  $s$  as the number of positive terms minus the number of negative terms,  $= 2p - r$ . Thus in the case of the Stuart and Matsen wave-functions the rank of the quadratic form is evidently 13, the index 5 and the signature (-)3. For the Anex functions, however, the quadratic form is apparently non-singular, its index is 1 and its signature (-)9. The case with the Anex and Shull coefficients, therefore, where the first coefficient is of different sign from the

rest, though very common does not happen invariably. HAGSTROM and SHULL<sup>(22,23)</sup> report a similar state of affairs for H<sub>2</sub>. A single-centre calculation yielded sixteen non-zero coefficients, of which four apart from the first were positive. Several of the positive coefficients were non-negligible. A two-centre calculation, however<sup>(24)</sup>, yielded the "usual" scheme, with the first coefficient of different sign from all the rest.

In order to compare the twelve wave-functions produced by Stuart and Matsen we have followed a method used by Anex and Shull. We look here for quantities which give a measure of the total "character" of a particular symmetry type in HeH<sup>+</sup>. The sum of the squares of the NSO coefficients corresponding to  $\sigma$ -configurations is called the total " $\Sigma$  character" of the molecule; the sum of the squares corresponding to  $\pi$ -configurations is called the total " $\Pi$  character"; and so on. In order to obtain some correspondence between the molecule and the atomic systems Li<sup>+</sup> and He, the total S character +  $\frac{1}{3}$  total P character +  $\frac{1}{5}$  total D character of the atomic systems is compared with the total  $\Sigma$  character of the molecule;  $\frac{2}{3}$  total P character +  $\frac{2}{5}$  total D character of the atomic systems is compared with the total  $\Pi$  character of the molecule; and so on. The S, P, etc., character comes from squaring the coefficients in the Li<sup>+</sup> and He natural expansions. Table III contains the results of this work. There is a smooth variation of each symmetry character so formulated, from Li<sup>+</sup> through the twelve different R-values to He. As

the  $\Sigma$  character decreases, each of the  $\Pi$  and  $\Delta$  characters shows a simultaneous increase. There is no minimum or maximum as was noticed with the  $c_1$  and  $c_2$  variation in Fig. 7. Thus, the  $c_1$  coefficient, though very large, is not completely dominant.

The corresponding values from the Anex and Shull natural expansions are, for  $R=1.0$  a.u.:  $\Sigma$ , 0.997927;  $\Pi$ , 0.002009;  $\Delta$ , 0.000058; and for  $R=1.4$  a.u.:  $\Sigma$ , 0.997799;  $\Pi$ , 0.002135;  $\Delta$ , 0.000060. These are extremely close to the Stuart and Matsen values, which is only to be expected since we noticed a very strong correspondence between the natural orbital coefficients themselves. In this manner, the rather gross approximation as regards the "character" as defined above gives us a slightly different way of looking at the comparison between the two wave-functions.

CHAPTER 4.

SUMMARY AND CONCLUSIONS.

This study of the molecular ion  $\text{HeH}^+$  has been instructive in several ways. By analysing the extensive configuration interaction wave-function of Stuart and Matsen we saw how a good one-centre calculation predicted the formation of the molecule. The density difference maps drawn at different bond lengths showed clearly that from being a one-centre system at large internuclear distances,  $\text{HeH}^+$  became more and more polarized as the proton approached the helium nucleus. The proton tended to take charge with it until it coincided with the helium nucleus, again forming a one-centre system.

The average values of  $r^n$  also showed clearly how the calculation predicted one-centre systems both at  $R=0$  and at  $R=\infty$ . They also showed that the proton greatly affected the density in the outer regions of the system, especially around an internuclear separation of about 2.5 a.u.. The conclusions from the density difference maps and expectation values are in line with the centre of charge calculations made by Peyerimhoff and by Anex. Their results showed that as the internuclear separation was increased, the electron cloud tended to follow the hydrogen nucleus at smaller  $R$ -values, and then showed a contraction towards the helium nucleus as  $R$  became relatively large.

Analysing the Stuart and Matsen functions in terms of natural orbitals made possible a comparison which would otherwise have been very difficult. We saw that this single-centre calculation and the two-centre calculation of Anex gave natural orbital coefficients which coincided to a very great degree of accuracy. It is worth bearing in mind that the Stuart and Matsen CI wave-function was composed from twenty-six basis orbitals, making thirty configurations, whereas the Anex CI wave-function had thirty-five configurations, made up from eleven basis orbitals. The natural expansion had the effect of reducing the number of natural orbital configurations in the Stuart and Matsen case from the expected twenty-six to thirteen, since thirteen coefficients were for all practical purposes zero. The thirteen which were not negligible were then found to be very close to the eleven from the Anex and Shull calculation. This similarity was evident both in the magnitudes of corresponding coefficients and in the symmetry of the basis orbitals from which they were composed. Hence, even though conceived and developed in entirely different ways, the two  $\text{HeH}^+$  calculations were shown to bear strong similarities to each other. This conclusion is in line with that of SHULL<sup>(21)</sup> as a result of his analysis of many varied hydrogen molecule calculations.

The density difference map in Fig. 4 gave information as to the effect of electron correlation in the Stuart and Matsen calculations. Here again we used as a basis the fact, noted by several authors and

confirmed by our own results in Part I, that the first natural orbital configuration bears a strong resemblance to the self-consistent-field function. Yet further evidence of this fact is given by Anex in the case of  $\text{HeH}^+$ . In addition to his CI work he made a SCF calculation, which for  $R=1.4$  a.u. gave an energy of  $-2.93192$  a.u.. (Peyerimhoff's SCF value was  $-2.93259$  a.u..) Calculating the energy from the first natural orbital configuration he obtained  $-2.93177$  a.u.. Using the truncated natural expansion as our uncorrelated function, we saw that the effect of correlation was to remove charge from the region between the nuclei and to pile it up on or behind them. In addition, there was a small increase of charge in the outer regions at right-angles to the internuclear axis on and around a line through the helium nucleus. These effects were noticed for all the bond lengths studied, from small to large values of  $R$ .

The average values of  $\cos \gamma_{12}$  appeared to give a rather sensitive measure of the electron correlation in both the atomic and molecular systems. In the first place, for He and  $\text{Li}^+$  a large difference between  $\langle \cos \gamma_{12} \rangle$  values was noticed for functions which differed by only about 4% in the predicted percentage correlation energy. Extension of this to the molecule explained why the limits of the  $\langle \cos \gamma_{12} \rangle$  versus  $R$  curve for the molecule did not tend to the atomic values. A rough calculation showed that the percentage correlation energy predicted for the molecule was considerably lower than that for the atoms. This seemed to explain why the whole curve was displaced towards higher

values of  $\langle \cos \gamma_{12} \rangle$ , i.e. towards lower corresponding values of  $\gamma_{12}$ .

The  $\langle \cos \gamma_{12} \rangle$  versus R curve calculated from the natural expansion "uncorrelated" function showed the expected behaviour at its limits. That is, it tended towards the atomic values of  $\langle \cos \gamma_{12} \rangle = 0$ ,  $\gamma_{12} = 90^\circ$ , for both the united atom  $\text{Li}^+$  and the separated system He. The curves for the uncorrelated function and the total function have relative positions indicating that on average the electrons are further apart in the latter case. This expected result is consistent with the charge movements noticed in the correlated minus uncorrelated density difference map and curves.

In their NSO paper on  $\text{HeH}^+$ , Anex and Shull discuss the resemblance between the first natural orbital configuration and the SCF function. They calculated the overlap between the first natural orbital and the SCF orbital, and found that there was a trend of increasing difference between the overlaps as R increased, and hence an increasing difference between the orbitals. Two possibilities were present; either the agreement between the orbitals increased with increasing atomic charge, or the agreement went through a minimum at or beyond  $R=2$  a.u.. Because of lack of evidence they were unable to choose between these alternatives. Our results from Part I, however, seemed to indicate that the effect of increasing Z was to draw the orbitals into better agreement. This of course does not preclude the possible existence of a minimum as described above.

Finally, a few words must be said on the great usefulness throughout this work of the natural expansion. It paid great dividends in Part I in giving a more detailed insight into the effects of radial and angular correlation. This was true to a lesser extent in Part II, but the technique came into its own when comparison was made between the superficially different functions of Stuart and Matsen and of Anex. In their original form no meaningful comparison is possible, but the natural expansion showed that in fact the functions were very similar, notably in the amount of  $\Sigma, \Pi$ , etc., "character" which each contained.

In a less direct but still very useful way, the natural expansion has paid dividends through uncovering mistakes in published data. In this connection we report two such errors. Firstly, in the  $H^-$  wave-function of WEISS<sup>(25)</sup>, p. 1829, Table I, the coefficient of the  $2p'3p'$  configuration should be 0.016493 and not 0.16493. Secondly, in the  $HeH^+$  function of Stuart and Matsen at  $R=1.2$  a.u., p. 1468, Table III, the coefficient of the  $1s5g$  configuration has the wrong sign. The nature of the natural expansion provides an immediate and relatively simple check on data as presented in journals etc.. A property such as this is extremely useful, since errors manage to creep into the literature with almost every extensive calculation. SHULL<sup>(21)</sup> goes so far as to suggest that one should perform an analysis of this kind wherever possible during the computations.

m	R=0.1			R=1.0			R=1.4		
	$\langle r^{-2} \rangle$	$\langle r \rangle$	$\langle r^4 \rangle$	$\langle r^{-2} \rangle$	$\langle r \rangle$	$\langle r^4 \rangle$	$\langle r^{-2} \rangle$	$\langle r \rangle$	$\langle r^4 \rangle$
1	27.467	1.1687	1.1442	12.734	1.6933	4.1091	11.835	1.8362	6.1884
2	27.486	1.1691	1.1461	12.738	1.6944	4.1026	11.841	1.8401	6.2592
3	27.463	1.1693	1.1459	12.722	1.6948	4.1197	11.825	1.8404	6.2561
4	27.453	1.1694	1.1458	12.724	1.6952	4.1245	11.828	1.8408	6.2619
5	27.452		1.1458	12.724		4.1246	11.828	1.8409	6.2626
6	27.454								6.2625

m	R=2.0			R=5.0		
	$\langle r^{-2} \rangle$	$\langle r \rangle$	$\langle r^4 \rangle$	$\langle r^{-2} \rangle$	$\langle r \rangle$	$\langle r^4 \rangle$
1	11.611	1.9279	9.1846	12.006	1.8580	7.7929
2	11.625	1.9351	9.2374	12.041	1.8617	7.9042
3	11.608	1.9354	9.2291	12.019	1.8622	7.8986
4	11.606	1.9356	9.2288	12.008	1.8625	7.8960
5	11.608	1.9357	9.2328	12.010	1.8626	7.9014
6						7.9017

Table I. Values of selected  $\langle r^n \rangle$  from the natural expansions of the Stuart and Matsen<sup>(8)</sup> wave-functions for HeH<sup>+</sup> truncated after m terms. The symmetry of the basis orbitals composing each natural orbital may be obtained from the tables of natural expansions at the end of Part II. Only the terms required for convergence to the values from the total wave-functions are shown. Values of bond length R are in atomic units.

$c_i$	R=1.0		R=1.4	
	STUART & MATSEN	ANEX & SHULL	STUART & MATSEN	ANEX & SHULL
1	0.996408 $\sigma$	0.996410 $\sigma$	0.995198 $\sigma$	0.995233 $\sigma$
2	-0.063610 $\sigma$	-0.062039 $\sigma$	-0.079150 $\sigma$	-0.077736 $\sigma$
3	0.043489 $\pi$	-0.043673 $\pi$	0.045027 $\pi$	-0.044962 $\pi$
4	-0.031859 $\sigma$	-0.033598 $\sigma$	-0.031345 $\sigma$	-0.033406 $\sigma$
5	-0.007718 $\sigma$	-0.007758 $\sigma$	-0.010792 $\sigma$	-0.009601 $\sigma$
6	0.007403 $\pi$	-0.007736 $\pi$	0.007862 $\pi$	-0.008359 $\pi$
7	-0.006320 $\delta$	-0.007294 $\delta$	-0.006575 $\delta$	-0.007476 $\delta$
8	0.005914 $\pi$	-0.006560 $\pi$	0.006307 $\pi$	-0.006722 $\pi$
9	-0.003990 $\sigma$	-0.006332 $\sigma$	-0.005044 $\sigma$	-0.006342 $\sigma$
10	-0.003048 $\sigma$	-0.004468 $\sigma$	-0.003946 $\sigma$	-0.004710 $\sigma$
11	-0.001077 $\sigma$	-0.002290 $\delta$	-0.001748 $\sigma$	-0.002311 $\delta$
12	-0.000309 $\pi$		-0.000403 $\pi$	
13	0.000141 $\pi$		0.000194 $\pi$	

Table II. Natural expansion coefficients and symmetry of basis orbitals composing the corresponding natural orbitals for the Stuart and Matsen<sup>(8)</sup> and the Anex<sup>(7)</sup> HeH<sup>+</sup> wave-functions. Values of bond length R are in atomic units.

Character	Li	0.1	0.5	1.0	1.2	1.3	1.4
$\Sigma$	0.998808	0.998689	0.998281	0.997972	0.997921	0.997850	0.997809
$\Pi$	0.001225	0.001267	0.001667	0.001979	0.002054	0.002090	0.002127
$\Delta$	0.000035	0.000029	0.000036	0.000039	0.000041	0.000042	0.000043

Character	1.5	1.6	2.0	3.0	4.0	5.0	He
$\Sigma$	0.997783	0.997790	0.997653	0.997448	0.997288	0.997244	0.997192
$\Pi$	0.002153	0.002183	0.002307	0.002557	0.002664	0.002696	0.002720
$\Delta$	0.000043	0.000044	0.000047	0.000054	0.000056	0.000058	0.000076

Table III. Symmetry "character" (for definition see text p.105) as calculated from the Stuart and Matsen<sup>(8)</sup> wave-functions. Values of bond length are in atomic units.

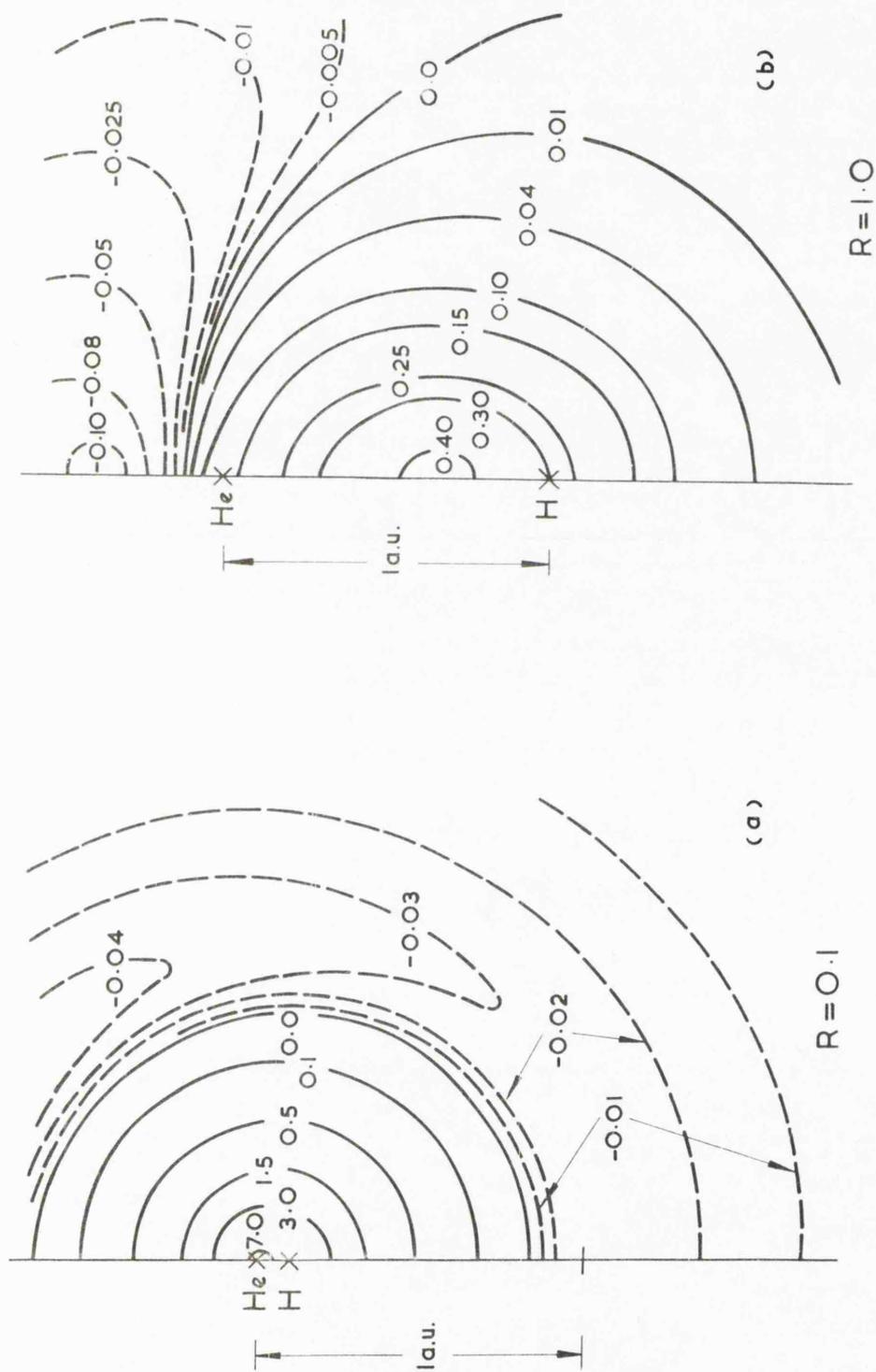


Fig. 1. Difference maps of the one-particle density from the total  $\text{HeH}^+$  functions minus that from the isolated He atom. The functions are those of Stuart and Matsen (8). Values of the bond length  $R$  are in atomic units.

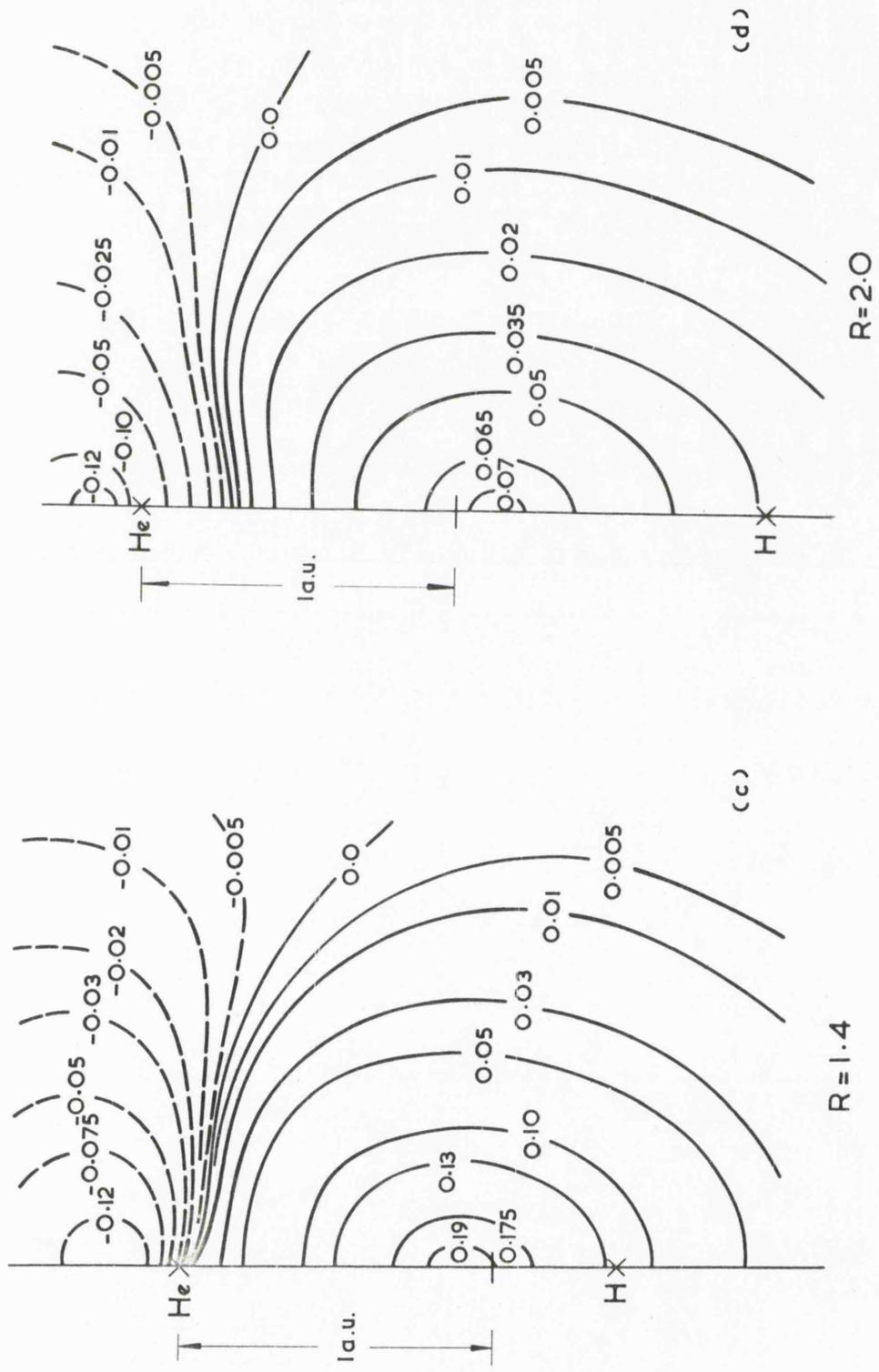


Fig. 1. Difference maps of the one-particle density from the total  $\text{HeH}^+$  functions minus that from the isolated He atom. The functions are those of Stuart and Matsen (8). Values of the bond length  $R$  are in atomic units.

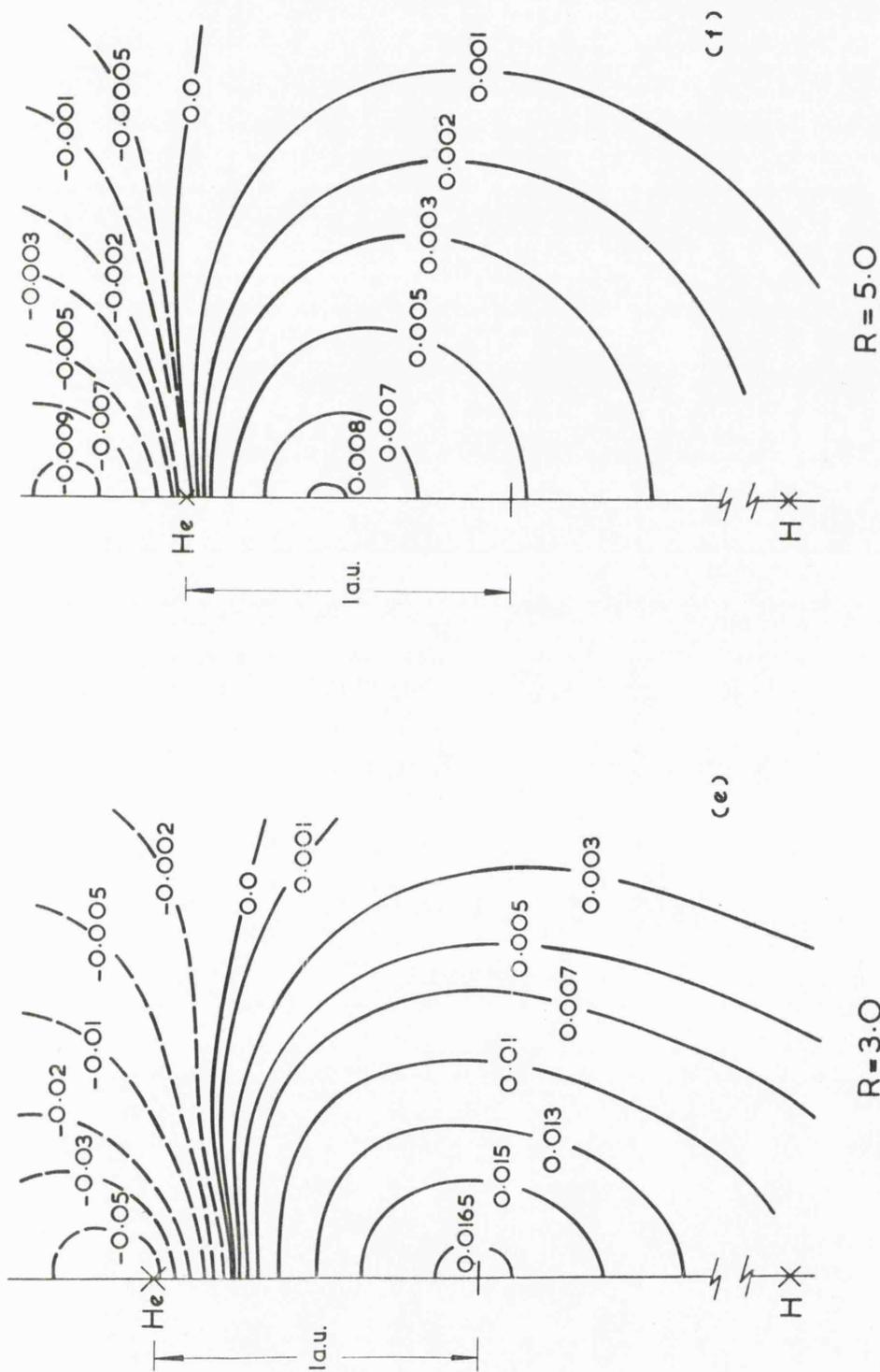


Fig. 1. Difference maps of the one-particle density from the total HeH<sup>+</sup> functions minus that from the isolated He atom. The functions are those of Stuart and Matsen (8). Values of the bond length R are in atomic units.

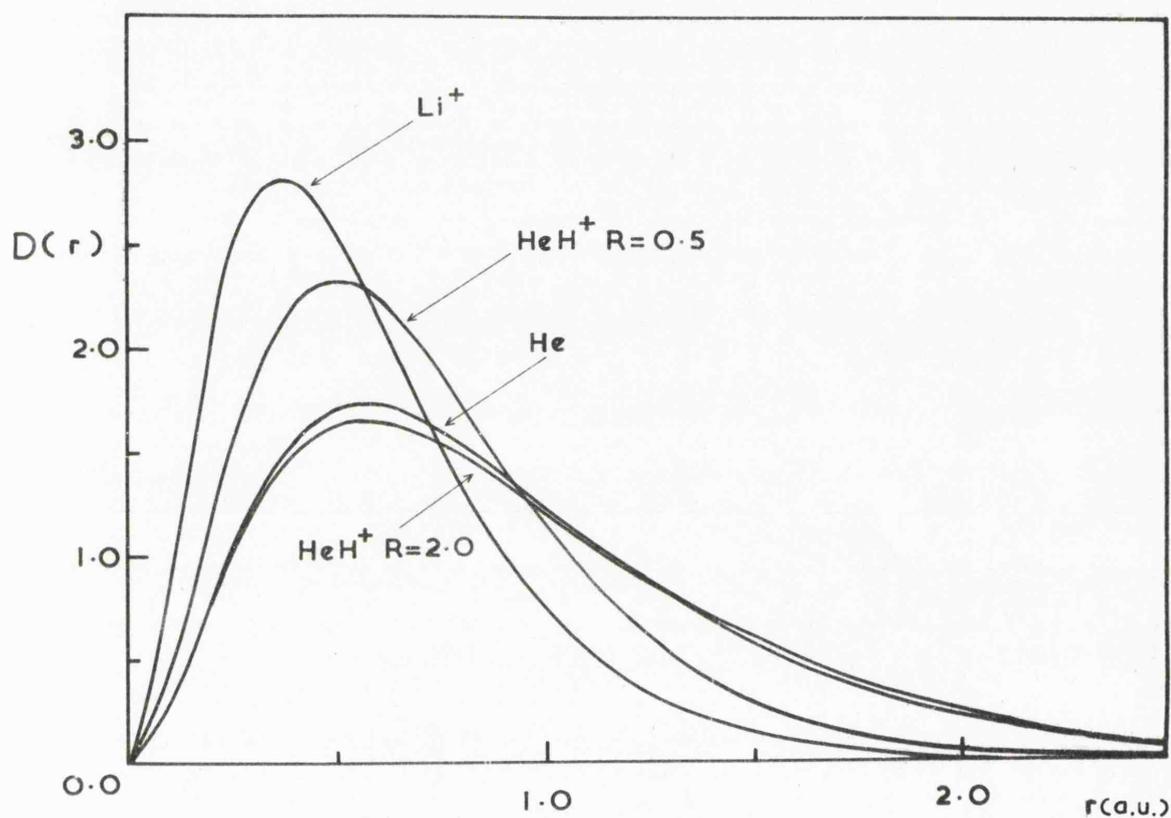


Fig. 2. Radial density distributions  $D(r)$  from the Stuart and Matsen  $\text{HeH}^+$ , He and  $\text{Li}^+$  wave-functions <sup>(8)</sup>. Values of bond length  $R$  are in atomic units.

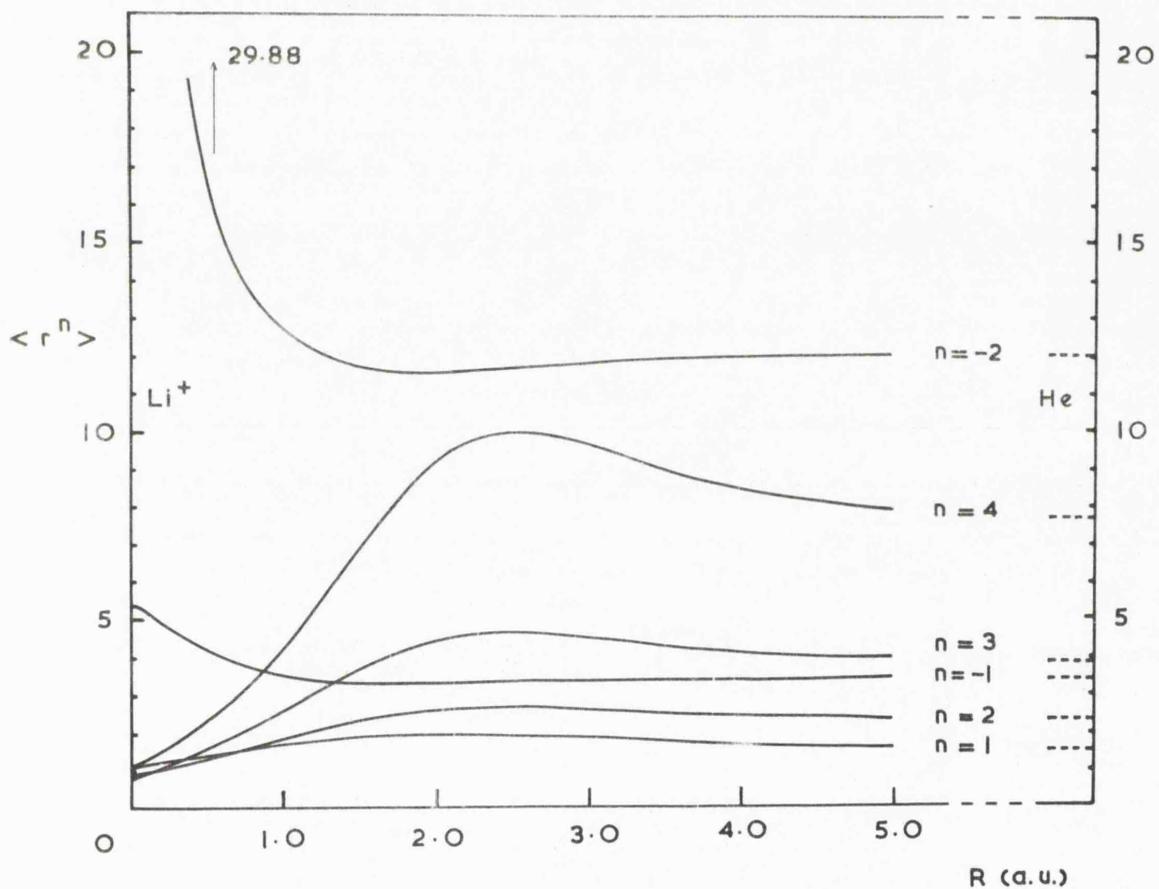


Fig. 3. Variation of  $\langle r^n \rangle$ ,  $-2 \leq n \leq 4$ , with bond length  $R$  for the Stuart and Matsen  $\text{HeH}^+$  wave-functions (8). The atomic values are also indicated.

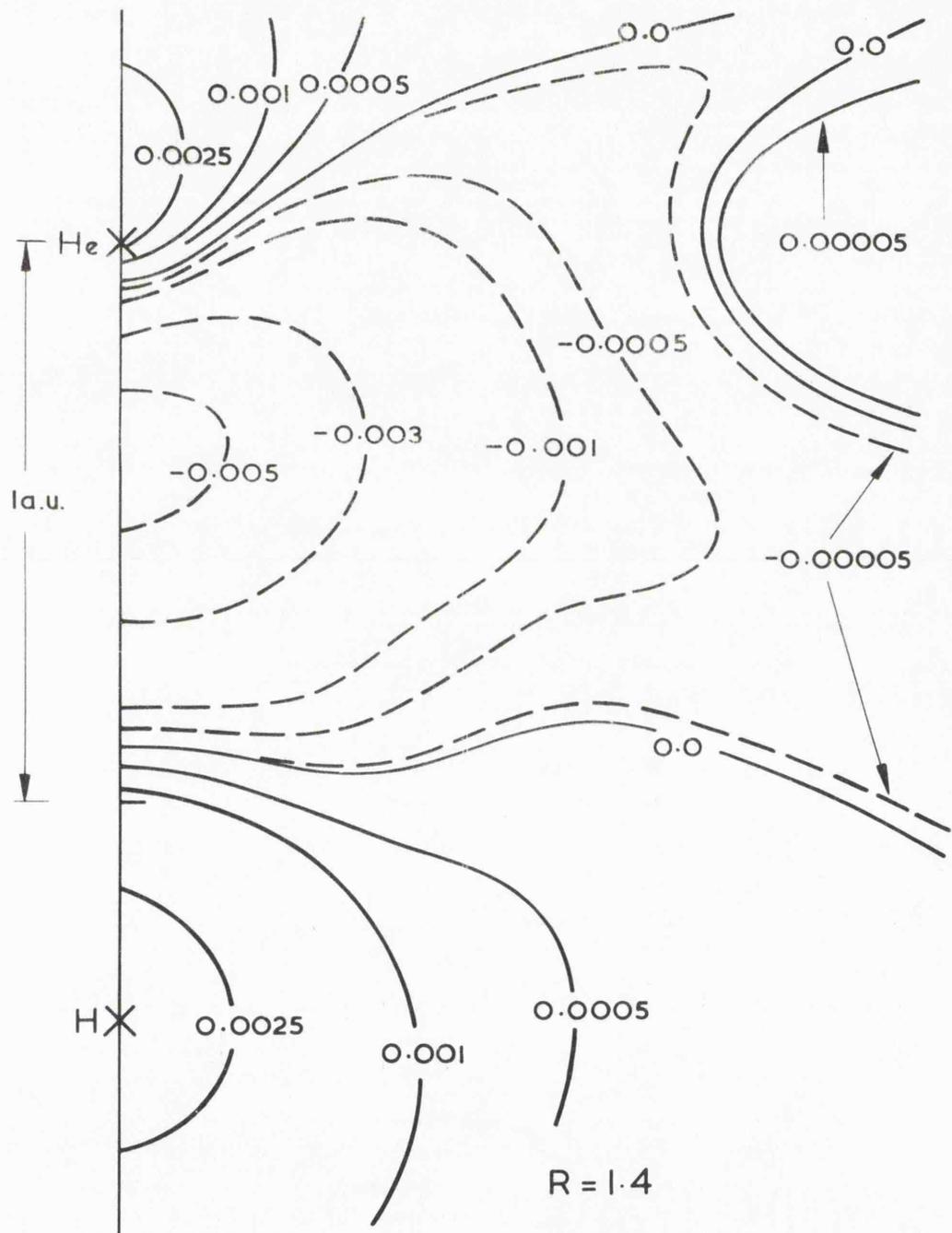


Fig. 4. Difference map of the one-particle density from the total HeH function minus that from the natural expansion truncated to the first configuration. The function is that of Stuart and Matsen<sup>(8)</sup> at a bond length of 1.4 a.u..

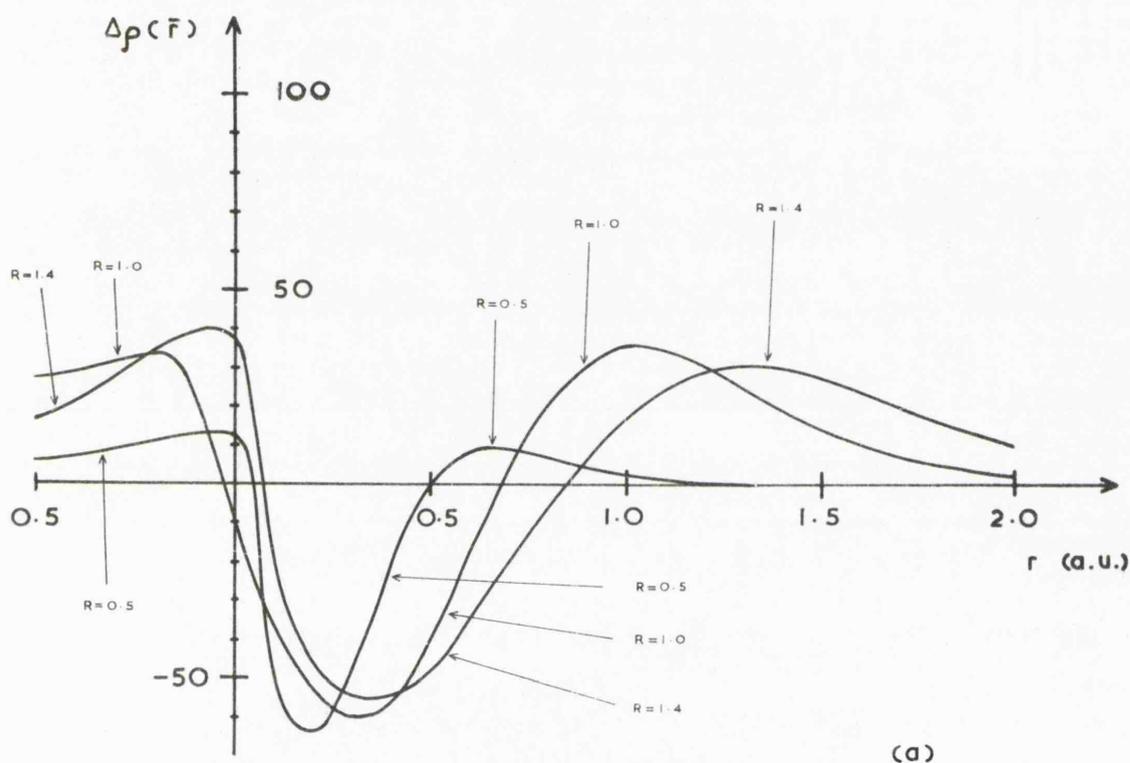


Fig. 5. Difference curves plotted along the internuclear axis of the one-particle density  $\Delta\rho(\bar{r})$  from the total  $\text{HeH}^+$  function minus that from the corresponding natural expansion truncated to the first configuration, for various bond lengths. Values of the bond length  $R$  are in atomic units. The He nucleus is situated at the origin. The  $\Delta\rho(\bar{r})$  values have been scaled up by a factor of  $10^4$ . The wave-functions are those of Stuart and Matsen <sup>(8)</sup>.

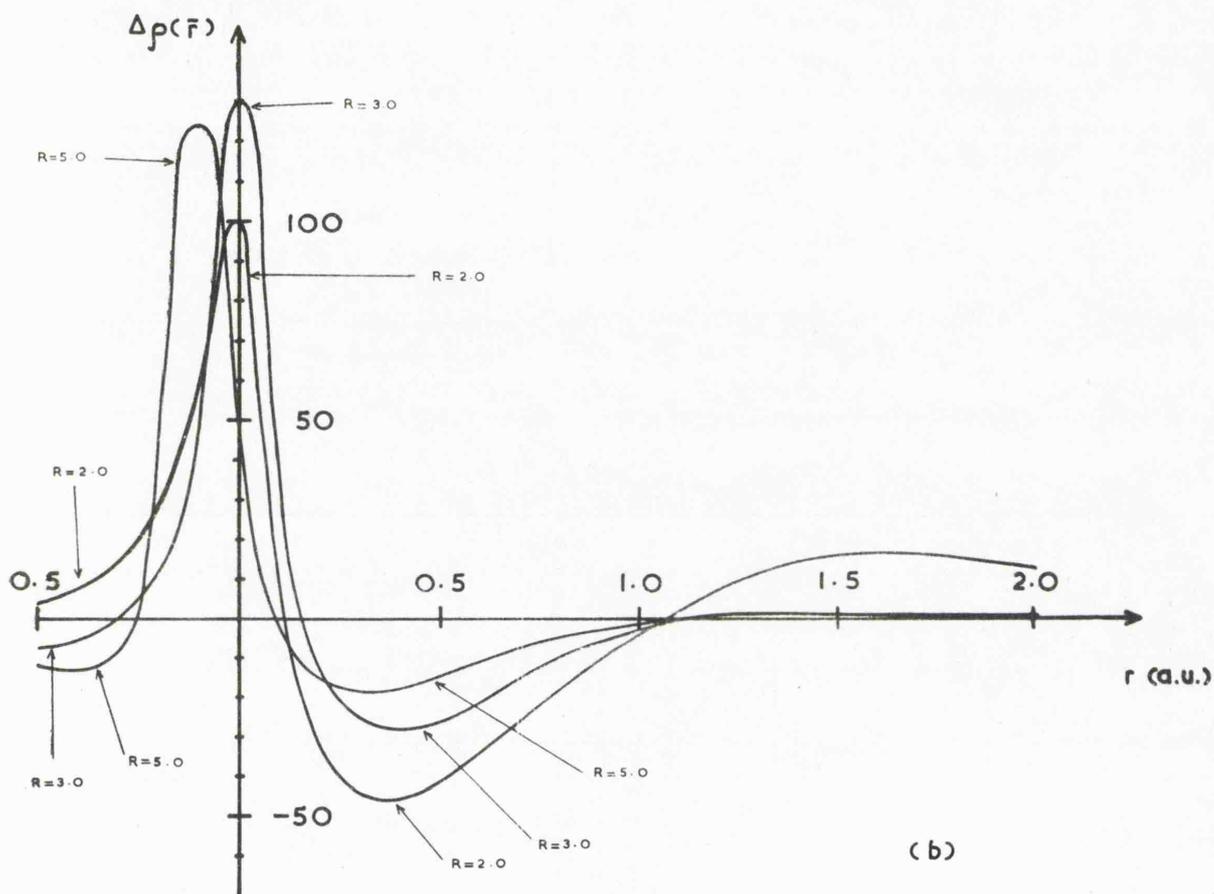


Fig. 5. Difference curves plotted along the internuclear axis of the one-particle density  $\Delta\rho(\bar{r})$  from the total  $\text{HeH}^+$  function minus that from the corresponding natural expansion truncated to the first configuration, for various bond lengths. Values of the bond length  $R$  are in atomic units. The He nucleus is situated at the origin. The  $\Delta\rho(\bar{r})$  values have been scaled up by a factor of  $10^4$ . The wave-functions are those of Stuart and Matsen<sup>(8)</sup>.

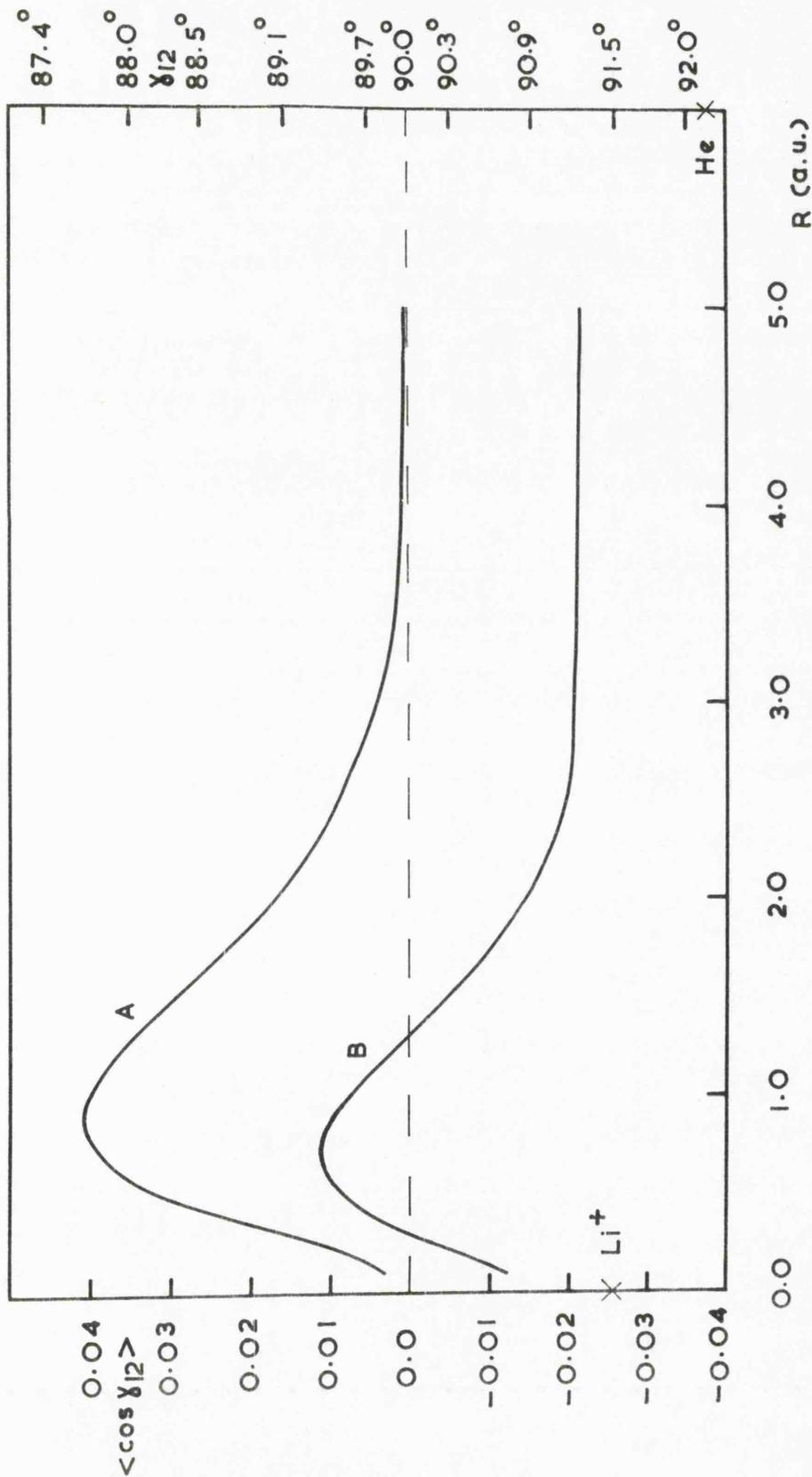


Fig. 6. Variation of  $\langle \cos \gamma_{12} \rangle$  for  $\text{HeH}^+$  with bond length  $R$  for the functions of Stuart and Matsen (8). Curve A corresponds to the natural expansions truncated to the first configuration and Curve B to the total wave-functions.

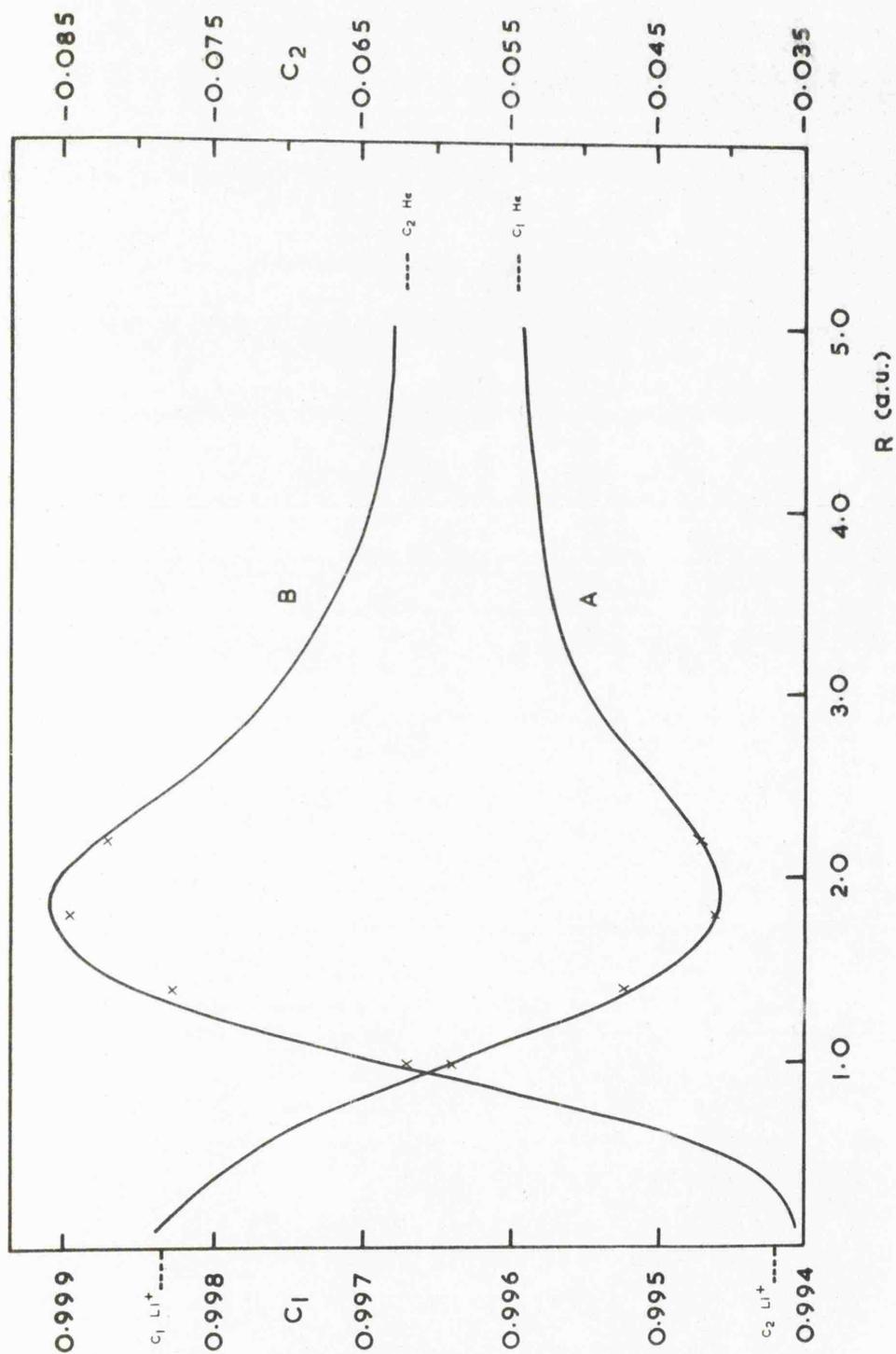


Fig. 7. Variation of the natural orbital coefficients  $c_1$  and  $c_2$  with bond length  $R$  for the Stuart and Matsen wave-functions (8). The crosses represent the results of Anax and Shull (17).

NATURAL EXPANSIONS FOR THE STUART & MATSEN FUNCTIONS.

In the following pages are presented the natural expansions of the wave-functions of Stuart & Matsen for He, Li<sup>+</sup>, and HeH<sup>+</sup> at twelve values of the internuclear distance. Alongside each coefficient is the symmetry of the basis orbitals composing the corresponding natural orbital. Within each natural orbital the basis orbitals are ordered as follows:

He, Li <sup>+</sup> :	1s	2s'	3s'		
	2p	3p	3d		
HeH <sup>+</sup> :	1s	2s'	3s'	2p	3p
	4p	3d	4d	4f	5f
	5g	6g	6h	7i	8j
	9k	10l	2p''	3p''	3d''
	2p'''	3p'''	3d'''	2p''''	3d''''
	3d''''				

NATURAL EXPANSION STUART & MATSEN He.

COEFFICIENTS:           1.   0.99596       s  
                          2.  -0.06200       s  
                          3.  -0.03597       p  
                          4.  -0.00727       s  
                          5.  -0.00585       p  
                          6.  -0.00539       d

NATURAL ORBITALS:

1.	1.23261	-0.26778	0.03026
	0.00000	0.00000	0.00000
2.	-1.92219	0.80919	1.44096
	0.00000	0.00000	0.00000
3.	0.00000	0.00000	0.00000
	0.45118	0.57103	0.00000
4.	-4.32703	6.79347	-2.69049
	0.00000	0.00000	0.00000
5.	0.00000	0.00000	0.00000
	-2.40758	2.38200	0.00000
6.	0.00000	0.00000	0.00000
	0.00000	0.00000	1.00000

NATURAL EXPANSION STUART & MATSEN Li<sup>+</sup>.

COEFFICIENTS:           1.   0.99836    s  
                          2.  -0.03700    s  
                          3.  -0.02404    p  
                          4.  -0.00447    s  
                          5.  -0.00396    p  
                          6.  -0.00380    d

NATURAL ORBITALS:

1.	1.13926	-0.14985	0.00657
	0.00000	0.00000	0.00000
2.	-1.79229	0.51275	1.59749
	0.00000	0.00000	0.00000
3.	0.00000	0.00000	0.00000
	0.42442	0.59743	0.00000
4.	-4.48366	6.79497	-2.51687
	0.00000	0.00000	0.00000
5.	0.00000	0.00000	0.00000
	-2.41244	2.37552	0.00000
6.	0.00000	0.00000	0.00000
	0.00000	0.00000	1.00000

NATURAL EXPANSION HeH<sup>+</sup> R = 0.1

COEFFICIENTS:	1.	0.99839	$\sigma$
	2.	-0.03559	$\sigma$
	3.	0.03476	$\pi$
	4.	-0.02430	$\sigma$
	5.	0.00564	$\pi$
	6.	-0.00547	$\delta$
	7.	0.00537	$\pi$
	8.	-0.00393	$\sigma$
	9.	-0.00388	$\sigma$
	10.	-0.00368	$\sigma$
	11.	-0.00006	$\sigma$
	12.	-0.00000	$\pi$
	13.	0.00000	$\pi$

NATURAL ORBITALS:

1.	1.11564	-0.04010	-0.08970	0.06064	-0.05401
	0.04860	0.00419	-0.00003	0.00101	0.00001
	-0.00019	0.00056	0.00020	0.00011	0.00007
	0.00005	0.00003	-0.00041	-0.00064	-0.00001
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	-1.59027	-0.16729	2.06620	-0.09563	0.08518
	-0.07664	-0.00660	0.00005	-0.00159	-0.00002
	0.00030	-0.00088	-0.00032	-0.00017	-0.00011
	-0.00008	-0.00005	-0.04281	-0.08776	-0.00035
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.40888	0.60926	0.00802	0.00214	0.04236
	0.00000				

4.	-0.29243	-0.14554	0.45619	0.08863	-0.07894
	0.07103	0.00612	-0.00004	0.00148	0.00001
	-0.00028	0.00082	0.00029	0.00016	0.00010
	0.00007	0.00004	0.27308	0.65348	0.00050
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.84008	1.99404	-0.58000	-0.15474	-0.01041
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.58077	1.28778	0.83057	0.22155	-0.02508
	0.00000				
8.	1.09123	-1.41316	0.32885	0.10950	-0.09754
	0.08776	0.00756	-0.00005	0.00182	0.00002
	-0.00034	0.00101	0.00036	0.00020	0.00013
	0.00009	0.00005	0.88700	-0.95585	0.88546
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				

9.	-2.03299	2.61832	-0.59969	-0.16335	0.14551
	-0.13091	-0.01128	0.00008	-0.00272	-0.00003
	0.00051	-0.00151	-0.00054	-0.00030	-0.00019
	-0.00013	-0.00008	-1.78375	1.86842	0.46319
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	-4.38966	5.54436	-1.19682	-0.02227	0.01984
	-0.01785	-0.00154	0.00001	-0.00037	-0.00000
	0.00007	-0.00021	-0.00007	-0.00004	-0.00003
	-0.00002	-0.00001	1.16651	-1.10134	0.01075
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	0.10087	-0.09573	-0.00027	-7.36750	6.56277
	-5.90459	-0.50875	0.00364	-0.12263	-0.00121
	0.02307	-0.06799	-0.02428	-0.01336	-0.00850
	-0.00607	-0.00364	5.33888	0.58752	0.22030
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-20.16945	-13.25177	13.32346	32.72651	-13.34677
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-20.17522	-13.24977	-13.33166	32.72691	13.34673
	0.00000				

NATURAL EXPANSION HeH+ R = 0.5

COEFFICIENTS:	1.	0.99779	$\sigma$
	2.	0.03995	$\pi$
	3.	-0.03734	$\sigma$
	4.	-0.03533	$\sigma$
	5.	0.00645	$\pi$
	6.	-0.00600	$\delta$
	7.	0.00557	$\pi$
	8.	-0.00491	$\sigma$
	9.	-0.00446	$\sigma$
	10.	-0.00379	$\sigma$
	11.	-0.00012	$\sigma$
	12.	-0.00010	$\pi$
	13.	0.00005	$\pi$

NATURAL ORBITALS:

1.	0.90568	0.10197	-0.02153	0.03723	0.11862
	0.00055	-0.00071	0.04806	-0.00578	0.02353
	-0.00506	0.01314	0.00453	0.00264	0.00166
	0.00111	0.00076	-0.00077	-0.00083	-0.00019
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.32786	0.65107	0.03188	0.02512	0.14218
	0.00000				
3.	-1.32364	0.37022	0.98495	0.13413	0.42736
	0.00200	-0.00257	0.17315	-0.02081	0.08477
	-0.01824	0.04736	0.01632	0.00951	0.00599
	0.00399	0.00274	0.10700	0.10835	0.02039
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				

4.	0.91684	0.35622	-1.60770	0.09695	0.30892
	0.00144	-0.00185	0.12516	-0.01504	0.06128
	-0.01319	0.03423	0.01180	0.00688	0.00433
	0.00288	0.00198	0.08374	0.08446	0.01568
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-0.47981	-0.57538	1.12775	0.86206	-0.14866
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-2.39840	2.39841	-0.07948	-0.06041	0.02002
	0.00000				
8.	-0.30841	0.43064	-0.13731	0.03607	0.11492
	0.00054	-0.00069	0.04656	-0.00560	0.02280
	-0.00491	0.01273	0.00439	0.00256	0.00161
	0.00107	0.00074	-2.41262	2.15267	0.20272
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				

9.	-0.93173	1.30649	-0.41452	0.07245	0.23085
	0.00108	-0.00139	0.09353	-0.01124	0.04579
	-0.00986	0.02558	0.00882	0.00514	0.00323
	0.00216	0.00148	0.42266	-0.96972	0.81887
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	-4.64543	6.55544	-2.06509	0.00995	0.03171
	0.00015	-0.00019	0.01285	-0.00154	0.00629
	-0.00135	0.00351	0.00121	0.00071	0.00044
	0.00030	0.00020	-0.00092	-0.06583	-0.23089
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	0.10668	-0.15631	0.04753	1.68525	5.36963
	0.02508	-0.03224	2.17551	-0.26147	1.06515
	-0.22924	0.59503	0.20506	0.11954	0.07522
	0.05015	0.03448	-2.70874	-4.48707	-2.19641
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	3.24195	7.12156	-4.01292	-10.21752	4.13193
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-3.40796	-7.50459	-3.91721	10.71680	3.95116
	0.00000				

NATURAL EXPANSION HeH+ R = 1.0

COEFFICIENTS:	1.	0.99641	$\sigma$
	2.	-0.06361	$\sigma$
	3.	0.04349	$\pi$
	4.	-0.03186	$\sigma$
	5.	-0.00772	$\sigma$
	6.	0.00740	$\pi$
	7.	-0.00632	$\delta$
	8.	0.00591	$\pi$
	9.	-0.00399	$\sigma$
	10.	-0.00305	$\sigma$
	11.	-0.00108	$\sigma$
	12.	-0.00031	$\pi$
	13.	0.00014	$\pi$

NATURAL ORBITALS:

1.	0.89801	-0.04536	0.14640	0.02672	0.01612
	0.14626	-0.01564	0.09405	-0.01642	0.05328
	-0.01317	0.03219	0.01131	0.00686	0.00440
	0.00296	0.00207	0.00004	-0.00213	-0.00022
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	-0.96883	-0.21937	1.16792	0.08715	0.05259
	0.47709	-0.05102	0.30678	-0.05355	0.17379
	-0.04297	0.10499	0.03689	0.02238	0.01435
	0.00965	0.00675	0.00195	0.14143	0.01219
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.33306	0.63391	0.03761	0.03275	0.16127
	0.00000				

4.	1.11217	0.06529	-1.47594	0.05246	0.03166
	0.28720	-0.03072	0.18468	-0.03224	0.10462
	-0.02587	0.06320	0.02221	0.01347	0.00864
	0.00581	0.00406	0.01145	0.24171	0.01561
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	-0.28636	0.27488	0.06098	-0.11342	-0.06844
	-0.62091	0.06641	-0.39927	0.06969	-0.22618
	0.05592	-0.13664	-0.04802	-0.02913	-0.01868
	-0.01257	-0.00878	0.34220	0.85427	-0.23648
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.10799	0.05473	1.03549	0.84063	-0.13533
	0.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-2.15510	2.57916	-0.52259	-0.41491	0.16352
	0.00000				

9.	-4.73831	6.73793	-2.16618	0.00209	0.00126
	0.01145	-0.00122	0.00736	-0.00128	0.00417
	-0.00103	0.00252	0.00089	0.00054	0.00034
	0.00023	0.00016	-0.01136	-0.00395	0.06036
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	0.19784	-0.31042	0.13449	-0.07725	-0.04662
	-0.42290	0.04523	-0.27194	0.04747	-0.15405
	0.03809	-0.09306	-0.03270	-0.01984	-0.01272
	-0.00856	-0.00598	0.65324	-0.11278	0.99246
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	0.03557	-0.06856	0.04401	-0.14608	-0.08815
	-0.79968	0.08553	-0.51422	0.08976	-0.29130
	0.07202	-0.17598	-0.06184	-0.03751	-0.02406
	-0.01618	-0.01131	-2.69781	3.32638	0.46656
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.11543	5.49706	-2.56198	-6.61534	2.75419
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.14104	-6.11103	-2.51197	7.18039	2.56201
	0.00000				

NATURAL EXPANSION HeH+ R = 1.2

COEFFICIENTS:	1.	0.99574	$\sigma$
	2.	-0.07284	$\sigma$
	3.	0.04428	$\pi$
	4.	-0.03155	$\sigma$
	5.	-0.00941	$\sigma$
	6.	0.00766	$\pi$
	7.	-0.00645	$\delta$
	8.	0.00607	$\pi$
	9.	-0.00459	$\sigma$
	10.	-0.00352	$\sigma$
	11.	-0.00140	$\sigma$
	12.	-0.00037	$\pi$
	13.	0.00017	$\pi$

NATURAL ORBITALS:

1.	0.89170	-0.06857	0.18653	0.03107	-0.01193
	0.16825	-0.01921	0.10238	-0.01977	0.06101
	-0.01574	0.03785	0.01342	0.00826	0.00535
	0.00362	0.00252	-0.00001	-0.00254	-0.00024
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	-0.99069	-0.10902	1.10826	0.09400	-0.03608
	0.50900	-0.05813	0.30973	-0.05981	0.18456
	-0.04762	0.11451	0.04061	0.02498	0.01619
	0.01095	0.00764	0.00603	0.13984	0.01069
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.34608	0.62627	0.03489	0.02978	0.15433
	0.00000				

4.	1.20269	-0.46031	-1.02896	0.05446	-0.02090
	0.29493	-0.03368	0.17946	-0.03466	0.10694
	-0.02759	0.06635	0.02353	0.01447	0.00938
	0.00635	0.00442	0.03345	0.33398	0.01552
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	-0.69337	0.89924	-0.16043	-0.13337	0.05119
	-0.72221	0.08248	-0.43946	0.08487	-0.26187
	0.06757	-0.16247	-0.05762	-0.03544	-0.02297
	-0.01554	-0.01083	0.40022	0.75971	-0.19699
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.21976	0.26275	0.97434	0.76053	-0.10038
	0.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-2.08990	2.56482	-0.59901	-0.45379	0.17886
	0.00000				

9.	-4.17501	6.76543	-2.89603	0.00931	-0.00357
	0.05039	-0.00575	0.03066	-0.00592	0.01827
	-0.00471	0.01134	0.00402	0.00247	0.00160
	0.00108	0.00076	-0.05465	-0.00173	0.15472
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	0.45841	-0.77900	0.37185	-0.07493	0.02876
	-0.40573	0.04633	-0.24689	0.04768	-0.14712
	0.03796	-0.09128	-0.03237	-0.01991	-0.01290
	-0.00873	-0.00609	0.72341	-0.28133	0.97254
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	0.12004	-0.22354	0.12717	-0.16128	0.06190
	-0.87335	0.09974	-0.53144	0.10263	-0.31668
	0.08171	-0.19648	-0.06967	-0.04286	-0.02778
	-0.01879	-0.01310	-2.63673	3.22901	0.46385
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.81261	5.16263	-2.22086	-6.00426	2.43110
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-0.79925	-5.88105	-2.16356	6.63192	2.22407
	0.00000				

NATURAL EXPANSION HeH+ R = 1.3

COEFFICIENTS:	1.	0.99545	$\sigma$
	2.	-0.07603	$\sigma$
	3.	0.04463	$\pi$
	4.	-0.03170	$\sigma$
	5.	-0.01018	$\sigma$
	6.	0.00778	$\pi$
	7.	-0.00650	$\delta$
	8.	0.00616	$\pi$
	9.	-0.00485	$\sigma$
	10.	-0.00374	$\sigma$
	11.	-0.00157	$\sigma$
	12.	-0.00038	$\pi$
	13.	0.00018	$\pi$

NATURAL ORBITALS:

1.	0.89118	-0.07693	0.20072	0.03255	-0.02082
	0.17314	-0.02037	0.10466	-0.02090	0.06369
	-0.01677	0.04009	0.01429	0.00885	0.00576
	0.00391	0.00273	-0.00004	-0.00268	-0.00025
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	-1.00114	-0.04877	1.07205	0.09590	-0.06133
	0.51011	-0.06001	0.30834	-0.06156	0.18763
	-0.04941	0.11811	0.04209	0.02607	0.01697
	0.01152	0.00804	0.00822	0.14008	0.01022
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.35796	0.61827	0.03304	0.02763	0.14893
	0.00000				

4.	1.23394	-0.68812	-0.81889	0.05324	-0.03405
	0.28318	-0.03331	0.17117	-0.03418	0.10416
	-0.02743	0.06557	0.02337	0.01447	0.00942
	0.00640	0.00446	0.04840	0.37535	0.01485
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	-0.88342	1.24338	-0.32566	-0.14046	0.08983
	-0.74713	0.08789	-0.45160	0.09017	-0.27481
	0.07236	-0.17300	-0.06165	-0.03819	-0.02485
	-0.01688	-0.01177	0.42827	0.70240	-0.18314
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.29115	0.39531	0.93549	0.71063	-0.07897
	0.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-2.04419	2.54408	-0.64052	-0.47100	0.18316
	0.00000				

9.	-3.87559	6.62891	-3.11494	0.01391	-0.00890
	0.07401	-0.00871	0.04473	-0.00893	0.02722
	-0.00717	0.01714	0.00611	0.00378	0.00246
	0.00167	0.00117	-0.08725	0.00887	0.20160
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	0.55667	-0.98958	0.50352	-0.07277	0.04654
	-0.38704	0.04553	-0.23395	0.04671	-0.14236
	0.03749	-0.08962	-0.03193	-0.01978	-0.01287
	-0.00874	-0.00610	0.77134	-0.36772	0.95714
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	0.16939	-0.32401	0.18831	-0.16735	0.10703
	-0.89016	0.10472	-0.53806	0.10743	-0.32742
	0.08622	-0.20611	-0.07345	-0.04550	-0.02961
	-0.02011	-0.01403	-2.60146	3.18244	0.46553
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.68608	5.03736	-2.11093	-5.76276	2.32597
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-0.64653	-5.75011	-2.06480	6.36002	2.12928
	0.00000				

NATURAL EXPANSION HeH+ R = 1.4

COEFFICIENTS:	1.	0.99520	$\sigma$
	2.	-0.07915	$\sigma$
	3.	0.04503	$\pi$
	4.	-0.03135	$\sigma$
	5.	-0.01079	$\sigma$
	6.	0.00786	$\pi$
	7.	-0.00657	$\delta$
	8.	0.00631	$\pi$
	9.	-0.00504	$\sigma$
	10.	-0.00395	$\sigma$
	11.	-0.00175	$\sigma$
	12.	-0.00040	$\pi$
	13.	0.00019	$\pi$

NATURAL ORBITALS:

1.	0.88635	-0.08125	0.21601	0.03359	-0.02738
	0.17530	-0.02160	0.10616	-0.02187	0.06576
	-0.01782	0.04207	0.01500	0.00937	0.00613
	0.00416	0.00292	-0.00007	-0.00280	-0.00025
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	-1.01017	0.01069	1.03342	0.09699	-0.07906
	0.50617	-0.06236	0.30654	-0.06316	0.18989
	-0.05144	0.12147	0.04332	0.02705	0.01769
	0.01202	0.00844	0.01027	0.13927	0.00966
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.37443	0.60570	0.03091	0.02549	0.14363
	0.00000				

4.	1.23667	-0.86675	-0.62371	0.04888	-0.03984
	0.25509	-0.03143	0.15448	-0.03183	0.09570
	-0.02593	0.06122	0.02183	0.01363	0.00892
	0.00606	0.00425	0.06878	0.42513	0.01353
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	-1.07503	1.60592	-0.51130	-0.14609	0.11908
	-0.76238	0.09392	-0.46170	0.09512	-0.28601
	0.07748	-0.18295	-0.06525	-0.04075	-0.02664
	-0.01810	-0.01271	0.45648	0.63259	-0.17255
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.37480	0.54058	0.89901	0.66129	-0.06157
	0.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.98618	2.50056	-0.67204	-0.47644	0.17858
	0.00000				

9.	-3.56473	6.41307	-3.25801	0.01849	-0.01507
	0.09649	-0.01189	0.05843	-0.01204	0.03620
	-0.00981	0.02315	0.00826	0.00516	0.00337
	0.00229	0.00161	-0.12709	0.02926	0.25228
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	0.64376	-1.19814	0.64823	-0.06976	0.05686
	-0.36406	0.04485	-0.22048	0.04542	-0.13658
	0.03700	-0.08737	-0.03116	-0.01946	-0.01272
	-0.00864	-0.00607	0.82893	-0.46051	0.93685
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	0.22278	-0.44302	0.26773	-0.17270	0.14077
	-0.90128	0.11103	-0.54582	0.11245	-0.33812
	0.09160	-0.21629	-0.07713	-0.04817	-0.03150
	-0.02140	-0.01502	-2.56111	3.13416	0.46662
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.69384	4.95946	-1.92813	-5.69296	2.15372
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-0.66899	-5.85289	-1.83469	6.48187	1.91043
	0.00000				

NATURAL EXPANSION HeH+ R = 1.5

COEFFICIENTS:	1.	0.99493	$\sigma$
	2.	-0.08242	$\sigma$
	3.	0.04530	$\pi$
	4.	-0.03062	$\sigma$
	5.	-0.01117	$\sigma$
	6.	0.00791	$\pi$
	7.	-0.00663	$\delta$
	8.	0.00639	$\pi$
	9.	-0.00521	$\sigma$
	10.	-0.00416	$\sigma$
	11.	-0.00192	$\sigma$
	12.	-0.00040	$\pi$
	13.	0.00020	$\pi$

NATURAL ORBITALS:

1.	0.87625	-0.07862	0.23052	0.03383	-0.02972
	0.17335	-0.02199	0.10632	-0.02269	0.06725
	-0.01838	0.04340	0.01559	0.00980	0.00643
	0.00438	0.00308	-0.00012	-0.00287	-0.00025
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	-1.01660	0.07614	0.98379	0.09638	-0.08467
	0.49379	-0.06264	0.30287	-0.06464	0.19156
	-0.05235	0.12363	0.04442	0.02793	0.01833
	0.01249	0.00876	0.01345	0.13663	0.00920
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.37839	0.60599	0.02870	0.02294	0.13665
	0.00000				

4.	1.20751	-0.99414	-0.44300	0.03984	-0.03500
	0.20410	-0.02589	0.12519	-0.02672	0.07918
	-0.02164	0.05110	0.01836	0.01154	0.00758
	0.00516	0.00362	0.10245	0.47804	0.01139
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	-1.28116	2.01855	-0.73979	-0.14752	0.12960
	-0.75583	0.09588	-0.46360	0.09894	-0.29321
	0.08013	-0.18924	-0.06799	-0.04275	-0.02806
	-0.01912	-0.01341	0.50041	0.52793	-0.16891
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.39686	0.61386	0.87839	0.62013	-0.04774
	0.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.97047	2.46730	-0.67782	-0.46037	0.16906
	0.00000				

9.	-3.21620	6.09625	-3.33194	0.02204	-0.01936
	0.11291	-0.01432	0.06925	-0.01478	0.04380
	-0.01197	0.02827	0.01016	0.00639	0.00419
	0.00286	0.00200	-0.17708	0.06481	0.31438
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	0.72332	-1.41526	0.81519	-0.06511	0.05720
	-0.33362	0.04232	-0.20463	0.04367	-0.12942
	0.03537	-0.08353	-0.03001	-0.01887	-0.01238
	-0.00844	-0.00592	0.92713	-0.59084	0.90508
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	0.28333	-0.59252	0.37710	-0.17925	0.15747
	-0.91839	0.11650	-0.56330	0.12022	-0.35627
	0.09736	-0.22995	-0.08262	-0.05194	-0.03409
	-0.02323	-0.01630	-2.50184	3.09246	0.47943
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.62910	4.89613	-1.83327	-5.56884	2.06185
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-0.59324	-5.79106	-1.74264	6.35049	1.82449
	0.00000				

NATURAL EXPANSION HeH<sup>+</sup> R = 1.6

COEFFICIENTS:	1.	0.99480	$\sigma$
	2.	-0.08391	$\sigma$
	3.	0.04560	$\pi$
	4.	-0.03074	$\sigma$
	5.	-0.01156	$\sigma$
	6.	0.00800	$\pi$
	7.	-0.00669	$\delta$
	8.	0.00644	$\pi$
	9.	-0.00532	$\sigma$
	10.	-0.00434	$\sigma$
	11.	-0.00207	$\sigma$
	12.	-0.00044	$\pi$
	13.	0.00022	$\pi$

NATURAL ORBITALS:

1.	0.87321	-0.07797	0.23840	0.03423	-0.03296
	0.17145	-0.02229	0.10573	-0.02313	0.06801
	-0.01890	0.04446	0.01606	0.01016	0.00670
	0.00458	0.00321	-0.00015	-0.00290	-0.00025
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	-1.02807	0.13900	0.94345	0.09648	-0.09290
	0.48326	-0.06282	0.29801	-0.06519	0.19168
	-0.05327	0.12531	0.04527	0.02865	0.01888
	0.01291	0.00905	0.01565	0.13595	0.00884
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.38509	0.60306	0.02648	0.02077	0.13042
	0.00000				

4.	1.17963	-1.09296	-0.29505	0.03413	-0.03287
	0.17098	-0.02223	0.10544	-0.02306	0.06782
	-0.01885	0.04434	0.01602	0.01013	0.00668
	0.00457	0.00320	0.12921	0.51277	0.00955
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	-1.44072	2.38310	-0.97228	-0.14937	0.14383
	-0.74818	0.09726	-0.46138	0.10092	-0.29677
	0.08248	-0.19401	-0.07008	-0.04435	-0.02923
	-0.01998	-0.01402	0.52245	0.45033	-0.16109
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.45627	0.73705	0.83695	0.56904	-0.02699
	0.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.92601	2.42584	-0.71146	-0.46190	0.16887
	0.00000				

9.	-2.90598	5.74298	-3.31252	0.02471	-0.02379
	0.12377	-0.01609	0.07632	-0.01670	0.04909
	-0.01364	0.03209	0.01159	0.00734	0.00483
	0.00331	0.00232	-0.22425	0.10445	0.38033
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	0.80751	-1.64006	0.98677	-0.06193	0.05963
	-0.31021	0.04033	-0.19130	0.04185	-0.12304
	0.03420	-0.08044	-0.02906	-0.01839	-0.01212
	-0.00828	-0.00581	1.01027	-0.70125	0.87124
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	0.34800	-0.75196	0.49416	-0.18491	0.17805
	-0.92624	0.12041	-0.57119	0.12494	-0.36740
	0.10211	-0.24018	-0.08676	-0.05490	-0.03618
	-0.02474	-0.01735	-2.44534	3.03454	0.48170
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.44331	4.69183	-1.66929	-5.19620	1.91036
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-0.36179	-5.58307	-1.59860	5.92982	1.68930
	0.00000				

NATURAL EXPANSION HeH<sup>+</sup> R = 2.0

COEFFICIENTS:	1.	0.99459	$\sigma$
	2.	-0.08521	$\sigma$
	3.	0.04687	$\pi$
	4.	-0.03149	$\sigma$
	5.	-0.01193	$\sigma$
	6.	0.00809	$\pi$
	7.	-0.00690	$\delta$
	8.	0.00683	$\pi$
	9.	-0.00546	$\sigma$
	10.	-0.00488	$\sigma$
	11.	-0.00241	$\sigma$
	12.	-0.00040	$\pi$
	13.	0.00023	$\pi$

NATURAL ORBITALS:

1.	0.85495	-0.05103	0.24921	0.03334	-0.03479
	0.15072	-0.02111	0.09627	-0.02303	0.06577
	-0.01940	0.04492	0.01651	0.01072	0.00720
	0.00497	0.00351	-0.00026	-0.00269	-0.00020
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	-1.08037	0.39828	0.77395	0.09325	-0.09729
	0.42148	-0.05903	0.26923	-0.06441	0.18393
	-0.05426	0.12563	0.04617	0.02998	0.02012
	0.01390	0.00980	0.02593	0.12937	0.00714
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.41557	0.58660	0.01851	0.01241	0.10206
	0.00000				

4.	0.95094	-1.12855	0.04255	0.00941	-0.00982
	0.04254	-0.00596	0.02718	-0.00650	0.01857
	-0.00548	0.01268	0.00466	0.00303	0.00203
	0.00140	0.00099	0.25966	0.58353	0.00220
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	1.89672	-3.65903	1.94361	0.14201	-0.14816
	0.64189	-0.08990	0.41002	-0.09810	0.28011
	-0.08263	0.19133	0.07032	0.04566	0.03065
	0.02117	0.01493	-0.60098	-0.11321	0.13037
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-1.65829	1.14898	0.73043	0.40107	0.01366
	0.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.75016	-2.18967	0.76454	0.39912	-0.12210
	0.00000				

9.	-1.70393	3.88099	-2.62558	0.02181	-0.02276
	0.09860	-0.01381	0.06298	-0.01507	0.04303
	-0.01269	0.02939	0.01080	0.00701	0.00471
	0.00325	0.00229	-0.41340	0.32071	0.67651
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	0.97855	-2.26225	1.55897	-0.04024	0.04198
	-0.18188	0.02547	-0.11618	0.02780	-0.07937
	0.02341	-0.05421	-0.01992	-0.01294	-0.00868
	-0.00600	-0.00423	1.49501	-1.30320	0.64715
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	0.60306	-1.48578	1.10293	-0.21477	0.22408
	-0.97079	0.13597	-0.62011	0.14836	-0.42364
	0.12497	-0.28936	-0.10635	-0.06905	-0.04635
	-0.03201	-0.02258	-2.06638	2.69231	0.46094
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.38390	4.62768	-1.37115	-5.07005	1.62414
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-0.30399	-5.56137	-1.28911	5.85684	1.41312
	0.00000				

NATURAL EXPANSION HeH+ R = 3.0

COEFFICIENTS:	1.	0.99545	$\sigma$
	2.	-0.07116	$\sigma$
	3.	0.04936	$\pi$
	4.	-0.03478	$\sigma$
	5.	-0.01029	$\sigma$
	6.	0.00823	$\pi$
	7.	0.00737	$\delta$
	8.	-0.00737	$\pi$
	9.	-0.00567	$\sigma$
	10.	-0.00545	$\sigma$
	11.	-0.00147	$\sigma$
	12.	-0.00025	$\pi$
	13.	0.00019	$\pi$

NATURAL ORBITALS:

1.	0.84545	0.00399	0.22081	0.02374	-0.00948
	0.07063	-0.00843	0.04986	-0.01326	0.03813
	-0.01236	0.02835	0.01096	0.00751	0.00524
	0.00373	0.00268	-0.00025	-0.00147	-0.00007
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	-1.27986	0.94364	0.49716	0.06743	-0.02693
	0.20062	-0.02394	0.14163	-0.03765	0.10833
	-0.03511	0.08053	0.03115	0.02134	0.01489
	0.01059	0.00763	0.03831	0.10091	0.00310
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.44228	0.57512	0.00777	0.00303	0.05121
	0.00000				

4.	0.51522	-0.68946	0.10961	-0.00276	0.00110
	-0.00822	0.00098	-0.00581	0.00154	-0.00444
	0.00144	-0.00330	-0.00128	-0.00087	-0.00061
	-0.00043	-0.00031	0.42033	0.56154	-0.00028
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	-2.14852	4.90545	-3.23252	-0.10262	0.04098
	-0.30530	0.03643	-0.21552	0.05730	-0.16485
	0.05343	-0.12255	-0.04740	-0.03248	-0.02266
	-0.01611	-0.01160	0.58555	-0.26849	-0.06385
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-2.09231	1.90722	0.46934	0.13495	0.04095
	0.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.19254	-1.46403	0.89806	0.24522	-0.04402
	0.00000				
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				

9.	-0.79310	2.03601	-1.54134	0.00365	-0.00146
	0.01086	-0.00130	0.00767	-0.00204	0.00586
	-0.00190	0.00436	0.00169	0.00116	0.00081
	0.00057	0.00041	-2.19134	2.15277	0.04757
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	-0.21146	0.54603	-0.41599	0.00236	-0.00094
	0.00703	-0.00084	0.00496	-0.00132	0.00380
	-0.00123	0.00282	0.00109	0.00075	0.00052
	0.00037	0.00027	0.25283	-0.25540	0.98736
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	-0.50469	1.44912	-1.22802	0.29605	-0.11823
	0.88080	-0.10510	0.62179	-0.16532	0.47560
	-0.15416	0.35357	0.13674	0.09370	0.06537
	0.04648	0.03348	1.17643	-1.81804	-0.22487
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.08382	4.51179	-1.03438	-4.66428	1.29746
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00570	-5.07429	-1.00154	5.10037	1.18753
	0.00000				

NATURAL EXPANSION H<sub>2</sub>H<sup>+</sup> R = 4.0

COEFFICIENTS:	1.	0.99585	$\sigma$
	2.	-0.06448	$\sigma$
	3.	0.05039	$\pi$
	4.	-0.03580	$\sigma$
	5.	-0.00895	$\sigma$
	6.	0.00828	$\pi$
	7.	0.00758	$\pi$
	8.	-0.00754	$\delta$
	9.	-0.00587	$\sigma$
	10.	-0.00543	$\sigma$
	11.	-0.00046	$\sigma$
	12.	-0.00014	$\pi$
	13.	0.00012	$\pi$

NATURAL ORBITALS:

1.	0.85703	-0.00664	0.21903	0.01551	0.00946
	0.01933	0.00068	0.01722	-0.00401	0.01417
	-0.00446	0.01103	0.00460	0.00324	0.00233
	0.00170	0.00125	-0.00015	-0.00077	-0.00003
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	-1.40085	1.08861	0.50392	0.04205	0.02565
	0.05242	0.00185	0.04668	-0.01088	0.03843
	-0.01209	0.02991	0.01246	0.00879	0.00632
	0.00461	0.00338	0.02808	0.06261	0.00115
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.44666	0.57406	0.00414	0.00093	0.02837
	0.00000				

4.	0.29190	-0.37382	0.04319	-0.00055	-0.00034
	-0.00069	-0.00002	-0.00061	0.00014	-0.00050
	0.00016	-0.00039	-0.00016	-0.00011	-0.00008
	-0.00006	-0.00004	0.44355	0.56535	-0.00003
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	-2.39366	5.48817	-3.66319	-0.06552	-0.03997
	-0.08169	-0.00288	-0.07275	0.01696	-0.05989
	0.01883	-0.04661	-0.01942	-0.01370	-0.00986
	-0.00718	-0.00526	0.41443	-0.25972	-0.03011
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-2.28296	2.19999	0.29975	0.04828	0.02870
	0.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.76625	-0.92974	0.95824	0.14776	-0.01543
	0.00000				
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				

9.	0.49564	-1.22487	0.89616	-0.00189	-0.00115
	-0.00236	-0.00008	-0.00210	0.00049	-0.00173
	0.00054	-0.00134	-0.00056	-0.00039	-0.00028
	-0.00021	-0.00015	2.33789	-2.30831	-0.00702
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	-0.10299	0.25723	-0.19052	0.00131	0.00080
	0.00163	0.00006	0.00145	-0.00034	0.00119
	-0.00038	0.00093	0.00039	0.00027	0.00020
	0.00014	0.00010	0.05002	-0.05212	0.99817
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	-0.25316	0.71594	-0.60446	0.43452	0.26503
	0.54169	0.01911	0.48243	-0.11244	0.39713
	-0.12490	0.30906	0.12878	0.09084	0.06536
	0.04763	0.03489	0.99387	-1.73954	-0.14159
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.04515	4.61997	-0.98783	-4.72633	1.23936
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00741	-4.94249	-0.96972	4.97554	1.17745
	0.00000				

NATURAL EXPANSION HeH+ R = 5.0

COEFFICIENTS:	1.	0.99592	$\sigma$
	2.	-0.06297	$\sigma$
	3.	0.05071	$\pi$
	4.	-0.03599	$\sigma$
	5.	-0.00856	$\sigma$
	6.	0.00831	$\pi$
	7.	-0.00762	$\delta$
	8.	0.00761	$\pi$
	9.	-0.00588	$\sigma$
	10.	-0.00541	$\sigma$
	11.	-0.00013	$\sigma$
	12.	-0.00009	$\pi$
	13.	0.00008	$\pi$

NATURAL ORBITALS:

1.	0.85941	-0.01266	0.22194	0.01094	0.01189
	0.00276	0.00247	0.00540	-0.00044	0.00419
	-0.00108	0.00328	0.00145	0.00098	0.00000
	0.00000	0.00000	-0.00010	-0.00048	-0.00001
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
2.	-1.42678	1.07736	0.55022	0.02932	0.03187
	0.00740	0.00663	0.01448	-0.00117	0.01124
	-0.00289	0.00880	0.00390	0.00262	0.00000
	0.00000	0.00000	0.01877	0.04031	0.00054
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
3.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.45142	0.57023	0.00255	0.00036	0.01783
	0.00000				

4.	0.18291	-0.22521	0.01683	-0.00024	-0.00027
	-0.00006	-0.00006	-0.00012	0.00001	-0.00009
	0.00002	-0.00007	-0.00003	-0.00002	0.00000
	0.00000	0.00000	0.44656	0.57039	-0.00001
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
5.	-2.51570	5.70114	-3.76966	-0.04429	-0.04814
	-0.01117	-0.01001	-0.02187	0.00176	-0.01698
	0.00437	-0.01330	-0.00589	-0.00396	0.00000
	0.00000	0.00000	0.26947	-0.17909	-0.01498
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
6.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	-2.36119	2.31431	0.18228	0.01860	0.01966
	0.00000				
7.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	1.00000				
8.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.46949	-0.57631	0.98486	0.09602	-0.00612
	0.00000				

9.	0.32059	-0.77635	0.55753	-0.00109	-0.00119
	-0.00028	-0.00025	-0.00054	0.00004	-0.00042
	0.00011	-0.00033	-0.00015	-0.00010	0.00000
	0.00000	0.00000	2.33098	-2.35270	-0.00248
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
10.	-0.05198	0.12737	-0.09274	0.00054	0.00059
	0.00014	0.00012	0.00027	-0.00002	0.00021
	-0.00005	0.00016	0.00007	0.00005	0.00000
	0.00000	0.00000	0.01591	-0.01669	0.99958
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
11.	0.12707	-0.35595	0.29898	-0.61834	-0.67201
	-0.15598	-0.13977	-0.30526	0.02460	-0.23705
	0.06094	-0.18561	-0.08218	-0.05535	0.00000
	0.00000	0.00000	-1.09700	2.01810	0.12482
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000				
12.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.01775	4.65924	-0.96154	-4.73601	1.20900
	0.00000				
13.	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.00000	0.00000	0.00000	0.00000	0.00000
	0.01691	-4.86579	-0.95037	4.89473	1.16984
	0.00000				

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APPENDIX

The General Theory of Natural Spin-Orbitals:

In the configuration interaction (CI) approximation the normalized wave-function of a system of N electrons may be represented as a linear combination of Slater determinants:

$$\Psi(x_1, x_2, \dots, x_N) = \sum_K C_K \Psi_K(x_1, x_2, \dots, x_N) \quad A(1)$$

where

$$\Psi_K(x_1, x_2, \dots, x_N) = (N!)^{-1/2} \det(\psi_{k_1}, \psi_{k_2}, \dots, \psi_{k_N}) \quad A(2)$$

The elements  $\psi_k$  of the determinant in A(2) are in general spin-orbitals (molecular or atomic orbitals) <sup>(a)</sup>. Each of these determinants does not necessarily have the symmetry of the system of which A(1) is the approximate wave-function, but the determinants may be grouped into so-called "configurations", which do have this symmetry. (This latter is the usual way of representing a configuration interaction wave-function.)

Before the theory is developed further, it is necessary

(a) On a point of convention: if the suffices  $k_1, k_2$ , etc. in A(2) are arranged in numerical order, such that, for instance  $k_1 < k_2 < \dots < k_N$ , then the Slater determinants A(2) are called "ordered".

to introduce some notation:

Consider two of the Slater determinants from the set A(1).

Let them be  $\Psi_K$  and  $\Psi_L$  say, where

$$\Psi_K = (N!)^{-1/2} \det(\psi_{k_1}, \psi_{k_2}, \dots, \psi_{k_N})$$

A(3)

$$\Psi_L = (N!)^{-1/2} \det(\psi_{l_1}, \psi_{l_2}, \dots, \psi_{l_N}) .$$

The sets  $\psi_k$  and  $\psi_l$  are chosen from an extended basis set, whose members are in general non-orthogonal, so that we can define "non-orthogonality integrals" between them:

$$d(kl) = \int \psi_k^*(x_1) \psi_l(x_1) dx_1 .$$

A(4)

The integral between the two Slater determinants in A(3) may easily be shown to be  $N!$  times the integral of the product of the diagonal term in  $\Psi_K$  and the determinant in  $\Psi_L$  . This in turn reduces to the determinant whose elements are the various integrals defined in A(4). i.e.

$$\int \Psi_K^* \Psi_L (dx) = (N!)(N!)^{-1/2} (N!)^{-1/2} \int \psi_{k_1}^* \dots \psi_{k_N}^* \det[\psi_{l_1}, \dots, \psi_{l_N}] (dx)$$

(where the notation  $(dx)$  denotes integration over all co-ordinates)

$$= D_{KL} = \det[d(k)]. \quad A(5)$$

Thus, the element in the first row, first column of  $D_{KL}$  is

$$\int \psi_{k_1}^*(x_1) \psi_{l_1}(x_1) dx_1$$

the element in the first row, second column of  $D$  is

$$\int \psi_{k_1}^*(x_1) \psi_{l_2}(x_1) dx_1$$

and so on.

The (N-1)th-order cofactors of  $\psi_K$  and  $\psi_L$  are

$$\det_K(1|k) \quad \text{and} \quad \det_L(1|l) \quad A(6)$$

respectively, where the 1 indicates that the first row has been removed and the  $k(l)$  that the column containing a particular  $\psi_k(\psi_l)$  has been removed. (NB a cofactor is a signed minor.) The (N-1)th-order cofactor of  $D_{KL}$  is correspondingly denoted by

$$D_{KL}(k|l) \quad A(7)$$

Both  $\psi_K$  and  $\psi_L$  may be expanded about their first rows,

so that

$$\begin{aligned} \Psi_K &= (N!)^{-1/2} \sum_k^K \psi_k(x_1) \det_K(1|k), \\ \Psi_L &= (N!)^{-1/2} \sum_l^L \psi_l(x_1) \det_L(1|l). \end{aligned} \quad A(8)$$

The notation  $\sum_k^K$  indicates that the summation takes place only over the spin-orbitals  $\psi_k$  which the particular set K contains. It is worth noting that in the general case which we are considering, that of non-orthogonal basis functions, the Slater determinants such as  $\Psi_K$  are not normalized.

In a way similar to that in which A(5) was derived, we can show that, using A(6) and A(7),

$$\int \det_K(1|k) \det_L(1|l) (dx) = (N-1)! D_{KL}(k|l), \quad A(9)$$

an expression which relates the cofactors of the determinants  $\Psi_K$  and  $\Psi_L$  with those of the determinant  $D_{KL}$  of the non-orthogonality integrals A(4).

Now let us define the first-order reduced density matrix  $\gamma(x'_1|x_1)$  for the system represented by the normalized wave-function  $\Psi$  given in A(1). We have

$$\gamma(x'_1|x_1) = N \int \Psi^*(x'_1, x_2, \dots, x_N) \Psi(x_1, x_2, \dots, x_N) (dx'_1) \quad A(10)$$

The prime on the  $x_1$  coordinate indicates that, when calculating the expectation value of some operator, we put  $x_1'$  equal to  $x_1$  after the operation has been performed. The operator thus works simply on the unprimed co-ordinates. The notation  $(dx_1)$  indicates that the integration takes place over all coordinates except  $x_1$ .

According to A(10), we have for the total integral

$$\int \gamma(x_1' | x_1) dx_1 = N . \quad \text{A(11)}$$

Assuming that our normalized wave-function may be expanded according to A(1), we may now obtain an expression for the first-order reduced density matrix within this approximation for  $\psi$  :

Substituting in A(10) for  $\Psi$  from A(1):

$$\gamma(x_1' | x_1) = N \int \sum_K C_K^* \Psi_K^* \sum_L C_L \Psi_L (dx') .$$

Substituting from A(8) for  $\Psi_K$  and  $\Psi_L$  expanded about their first rows:

$$\begin{aligned} \gamma(x_1' | x_1) = & \frac{N}{N!} \int \sum_K \sum_k C_K^* \psi_k^*(x_1') \det_K(1|k) \times \\ & \times \sum_L \sum_l C_L \psi_l(x_1) \det_L(1|l) (dx') . \end{aligned} \quad \text{A(12)}$$

The double summation  $\sum_K \sum_k$ , for example, means:

for a particular set of spin-orbitals  $K$ , sum over all the  $\psi_k$  contained in that set, and then sum over all such sets  $K$ . This can clearly be re-arranged as  $\sum_k \sum_K^{(k)}$ , which means: for a particular spin-orbital  $\psi_k$  from the extended basis set, sum over all the sets  $K$  of spin-orbitals which contain that particular  $\psi_k$ , and then sum over all possible  $\psi_k$ . Using summations re-arranged in this way, A(12) becomes

$$\gamma(x'_1|x_1) = \frac{N}{N!} \int \sum_k \psi_k^*(x'_1) \sum_K^{(k)} C_K^* \det_K(l|k) \times \\ \times \sum_l \psi_l(x_1) \sum_L^{(l)} C_L \det_L(l|l) (dx'_1) .$$

Using A(9) this becomes

$$\gamma(x'_1|x_1) = \frac{N(N-1)!}{N!} \sum_{kl} \psi_k^*(x'_1) \psi_l(x_1) \sum_K \sum_L^{(kl)} C_K^* D_{KL}(k|l) C_L \\ \sum_{kl} \psi_k^*(x'_1) \gamma(l|k) \psi_l(x_1) \tag{A13}$$

where  $\gamma(l|k) = \sum_K \sum_L^{(kl)} C_K^* D_{KL}(k|l) C_L$  A(14)

$\gamma(l|k)$  is Löwdin's <sup>(a)</sup> "first-order density in the k-space".

(a) The general theory of natural spin-orbitals for an orthonormal basis set is given in: P.-O. Löwdin, Phys. Rev. 97, 1474 (1955).

It is a square matrix whose order is equal to the number of basis orbitals being used in the approximation of  $\Psi$ . The factor  $D_{KL}(k|l)$  is, of course, the (N-1)th-order cofactor of  $D_{KL}$ , remaining from  $D_{KL}$  after the row containing  $\psi_k$  and the column containing  $\psi_l$  have been removed. (see A(7)).

In order to obtain the natural spin-orbitals (NSO's) for the wave-function  $\Psi$  we need to derive the first-order reduced density matrix  $\gamma(x'_1|x_1)$  in the form given in A(13). This in turn requires the production of the matrix  $\gamma(l|k)$ , defined in A(14); it is this which proves the most tedious task, since it includes the evaluation of (N-1)th-order determinants in  $D_{KL}(k|l)$ .

The natural spin-orbitals are defined as being that orthogonal basis in which the first-order reduced density matrix is diagonal.

In general, the form of  $\gamma(x'_1|x_1)$  given in A(13) will contain some cross-terms. It will become diagonal if  $\gamma(l|k)$  be diagonal, i.e. only terms with  $k=l$  will remain. Thus, from the original extended basis  $\psi_k$ , we wish to obtain the NSO's by means of a linear transformation using some matrix A, as yet unknown. We wish this new basis to be orthonormal, and at the same time to render the first-order reduced density matrix into diagonal form. These stipulations may be represented mathematically:

$$\chi_l = \sum \psi_k A_{kl}$$

or, in matrix notation

$$\underline{\chi} = \underline{\psi} \underline{A} \quad \text{A(15)}$$

Here,  $\underline{\chi}$  represents a row-vector of the natural spin-orbitals and  $\underline{\psi}$  a row-vector of the original basis spin-orbitals.  $\underline{A}$  is the required transformation matrix, whose exact form we wish to find. Thus in general, each NSO  $\chi_l$  is a linear combination of the original basis spin-orbitals  $\psi_k$ , and there will be as many NSO's as there are basis orbitals.

The requirement that the  $\chi$ 's form an orthonormal set may be written

$$\int \chi_k^*(x_i) \chi_l(x_i) dx_i = \delta_{kl}$$

or

$$\langle \underline{\chi}^\dagger | \underline{\chi} \rangle = \underline{I} \quad \text{A(16)}$$

The notation  $\underline{\chi}^\dagger$  represents the complex conjugate of the transpose of  $\underline{\chi}$ , so that since  $\underline{\chi}$  is a row-vector,  $\underline{\chi}^\dagger$  is a column-vector;  $\underline{I}$  is the identity matrix.

Substituting for  $\underline{\chi}$  from A(15) in the condition A(16):

$$\langle \underline{A}^\dagger \underline{\psi}^\dagger \underline{\psi} \underline{A} \rangle = \underline{I}$$

i.e.  $\underline{A}^\dagger \underline{\Delta} \underline{A} = \underline{I}$  A(17)

where  $\underline{\Delta} = \langle \underline{\psi}^\dagger \underline{\psi} \rangle$  and is the "overlap matrix"; its elements are the various overlap integrals  $d(kl)$  defined in A(4). The orthogonality requirement for the  $\chi$ -basis thus leads to condition A(17).

We also require that, expressed in terms of this orthonormal basis, the first-order reduced density matrix be diagonal. Equation A(13) may be re-written in matrix notation as follows:

$$\gamma(x'_1 | x_1) = \underline{\psi} \underline{\gamma} \underline{\psi}^\dagger \quad \text{A(18)}$$

Now from A(15)

$$\underline{\psi} = \underline{\chi} \underline{A}^{-1}$$

and

$$\underline{\psi}^\dagger = (\underline{A}^{-1})^\dagger \underline{\chi}^\dagger$$

Substituting for  $\underline{\psi}$  and  $\underline{\psi}^\dagger$  in A(18):

$$\gamma(x'_1|x_1) = \underline{\chi} \underline{A}^{-1} \underline{\gamma} (\underline{A}^{-1})^\dagger \underline{\chi}^\dagger .$$

$\gamma(x'_1|x_1)$  will be diagonal in the  $\chi$ -basis if the matrix

$$\underline{A}^{-1} \underline{\gamma} (\underline{A}^{-1})^\dagger$$

be diagonal, i.e. if

$$\underline{A}^{-1} \underline{\gamma} (\underline{A}^{-1})^\dagger = \underline{n} \tag{A(19)}$$

where  $\underline{n}$  is a diagonal matrix. Then we may write

$$\gamma(x'_1|x_1) = \underline{\chi} \underline{n} \underline{\chi}^\dagger$$

or

$$\gamma(x'_1|x_1) = \sum_k \chi_k^*(x'_1) n_k \chi_k(x_1) \tag{A(20)}$$

in which form the first-order reduced density matrix is diagonal. A(20) leads to the following normalization condition from the total integral:

$$\sum_k n_k = N \tag{A(21)}$$

using equation A(11).

The diagonal elements  $n_k$  of the diagonal matrix  $\underline{n}$  are known as the "occupation numbers" of the natural spin-orbitals  $\chi_k$ .

To summarize, the two conditions which must be satisfied to obtain the transformation matrix  $\underline{A}$  and the matrix of the occupation numbers  $\underline{n}$  are

$$\underline{A}^\dagger \underline{\Delta} \underline{A} = \underline{I} \quad \text{A(21)(a)}$$

and

$$\underline{A}^{-1} \underline{\gamma} (\underline{A}^{-1})^\dagger = \underline{n} \quad \text{A(21)(b)}$$

Unlike the case described by Löwdin, our basis set of the spin-orbitals  $\psi_k$  is not an orthonormal one. In the orthonormal case,  $\underline{\Delta}$  becomes the identity matrix, so that A(21)(a) reduces to

$$\underline{A}^\dagger \underline{A} = \underline{I}$$

which is the condition that the matrix  $\underline{A}$  be unitary. In the case under discussion, therefore,  $\underline{A}$  is not unitary, and the two conditions A(21)(a) and A(21)(b) have to be satisfied simultaneously to find the unique transformation matrix  $\underline{A}$ .

One method of doing this is as follows:

Perform a unitary transformation on the overlap matrix  $\underline{\Delta}$  :

$$\underline{U}^\dagger \underline{\Delta} \underline{U} = \underline{I} \quad \text{A(22)}$$

Here,  $\underline{U}$  is a unitary matrix whose columns are the eigenvectors

of  $\underline{\Delta}$ .  $\underline{T}$  is a diagonal matrix (not in general the identity matrix) whose diagonal elements are the eigenvalues of  $\underline{\Delta}$ . Now let us define some matrix  $\underline{W}$ , whose elements are given by the relation

$$w_{ij} = \frac{u_{ij}}{\sqrt{t_{jj}}} \quad \text{A(23)}$$

By operating on  $\underline{\Delta}$  with  $\underline{W}$ , we are forcing out the identity matrix:

$$\underline{W}^\dagger \underline{\Delta} \underline{W} = \underline{I} \quad \text{A(24)}$$

Comparing A(21) (a) and A(24), it would appear that  $\underline{W}$  and  $\underline{A}$  are identical. This is not true, however, since in general,  $\underline{A}$  is given by the product of  $\underline{W}$  and some other matrix,  $\underline{X}$  say:

$$\underline{A} = \underline{W} \underline{X} \quad \text{and} \quad \underline{A}^\dagger = \underline{X}^\dagger \underline{W}^\dagger \quad \text{A(25)}$$

The nature of  $\underline{X}$  may be discovered by substituting from A(25) in A(21) (a):

$$\underline{X}^\dagger \underline{W}^\dagger \underline{\Delta} \underline{W} \underline{X} = \underline{I}$$

Using A(24) this becomes

$$\underline{X}^\dagger \underline{X} = \underline{I}$$

so that  $\underline{X}$  is a unitary matrix. Thus, any unitary matrix can be used, and A(24) will still be satisfied. To obtain the exact form of  $\underline{X}$  we use condition A(21)(b):

From A(25) 
$$\underline{A}^{-1} = \underline{X}^{-1} \underline{W}^{-1}$$

so that A(21)(b) becomes

$$\underline{X}^{-1} \underline{W}^{-1} \underline{y} (\underline{W}^{-1})^\dagger (\underline{X}^{-1})^\dagger = \underline{n} \tag{A(26)}$$

Putting  $\underline{W}^{-1} \underline{y} (\underline{W}^{-1})^\dagger = \underline{M}$ , say, and using the fact that  $\underline{X}$  is unitary, we obtain

$$\underline{X}^\dagger \underline{M} \underline{X} = \underline{n} \tag{A(27)}$$

If we perform this unitary transformation, we may obtain the diagonal matrix of the occupation numbers,  $\underline{n}$ . In addition, the columns of  $\underline{X}$  are formed from the eigenvectors of  $\underline{M}$ , so that we can obtain the product  $\underline{W}\underline{X}$ , which, as defined in A(25), is the required transformation matrix  $\underline{A}$ .

Using the quantities defined in this way, we may now expand the wave-function in terms of the natural spin-orbitals.

Determinants are formed with the NSO's as elements, and the so-called "natural expansion" of the wave-function is obtained in terms of these new Slater determinants.

When exactly  $N$  of the NSO's are fully occupied (i.e. have occupation numbers equal to 1) we have a limiting case, in which the natural expansion is reduced to a single Slater determinant. From a convergence point of view, this is obviously the most favourable case. Even if only a small number of the  $n_k$  are non-zero (some being essentially zero), then the natural expansion will only contain relatively few terms, leading to an improvement in the convergence of the wave-function. It can be shown that the introduction of the natural spin-orbitals leads to an expansion of most rapid convergence within the original basis.

(a)

The Case of Two Electrons:

The general NSO theory dealt with above undergoes some simplification in the special case of two-electron systems. The configuration interaction singlet-state normalized wave-function may in this case be written

(a) see, for example, P.-O. Löwdin and H. Shull, Phys. Rev. 101,1730 (1956).

$${}^1\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \sum_{kl} C_{kl} \det [\psi_k \alpha; \psi_l \beta] \quad A(29)$$

with  $C_{kl} = C_{lk}$ .

Here we can use the well-known fact that, with a two-electron wave-function the singlet spin function may be factored off from the determinants; re-writing A(29):

$${}^1\Psi(x_1, x_2) = \sum_{kl} C_{kl} \psi_k(\bar{r}_1) \psi_l(\bar{r}_2) \frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \quad A(30)$$

Formation of the first-order reduced density matrix (from A(10)) gives

$$\gamma(x'_1 | x_1) = (\alpha'\alpha + \beta'\beta) \sum_{kl} \psi_k^*(\bar{r}'_1) \gamma(l|k) \psi_l(\bar{r}_1) .$$

In this simplified case,  $\gamma(l|k)$  is in general a sum of products made up of coefficients and overlap integrals defined in A(4). (These overlap integrals have taken the place of the (N-1)th-order cofactors  $D_{KL}(k|l)$  in A(14); in this present case, of course,  $N-1 = 1$ .) In the particular case of an orthonormal basis, the matrix  $\underline{\gamma}$  simplifies further to

$$\underline{\gamma} = \underline{C} \underline{C}^\dagger$$

where  $\underline{C}$  is the coefficient matrix of the original configuration interaction wave-function. The formation of  $\underline{\gamma}$  is thus far simpler in the two-electron case than in the general N-electron case discussed above.

We have now to satisfy conditions A(21)(a) and A(21)(b). In doing so, we obtain matrices  $\underline{A}$  and  $\underline{n}$ , as before. By diagonalizing  $\underline{\gamma}$ , the first-order reduced density matrix becomes diagonal in the  $\underline{\chi}$ -basis. However, because of the particular nature of the two-electron configuration interaction wave-function, yet a further simplification is possible. The wave-function  ${}^1\Psi$  is a real quadratic form in the original basis, i.e.:

$${}^1\Psi = \underline{\psi} \underline{C} \underline{\psi}^\dagger \quad \text{A(31)}$$

where  $\underline{\psi}$  is again a row-vector of the basis spin-orbitals and  $\underline{C}$  is the matrix of the coefficients. Using the transformations

$$\underline{\psi} = \underline{\chi} \underline{A}^{-1} \quad \text{and} \quad \underline{\psi} = (\underline{A}^{-1})^\dagger \underline{\chi}^\dagger \quad \text{we have}$$

$${}^1\Psi = \underline{\chi} \underline{A}^{-1} \underline{C} (\underline{A}^{-1})^\dagger \underline{\chi}^\dagger .$$

Condition A(21)(b) is hence replaceable by

$$\underline{A}^{-1} \underline{C} (\underline{A}^{-1})^\dagger = \underline{c}$$

where  $\underline{c}$  is a diagonal matrix whose non-zero elements are the coefficients in the natural expansion, for then

$${}^1\Psi = \underline{\chi} \underline{c} \underline{\chi}^\dagger .$$

Thus, we have brought the wave-function itself to diagonal form in the  $\chi$ -basis. In this simplified case,

$${}^1\Psi = \sum_k c_k \chi_k^{*(1)} \chi_k^{(2)} \frac{\alpha^{(1)}\beta^{(2)} - \alpha^{(2)}\beta^{(1)}}{\sqrt{2}} \quad A(32)$$

where the  $c_k$  are the diagonal elements of  $\underline{c}$ . This form is to be compared with that in A(30). Now, within the  $\chi$ -basis the first-order reduced density matrix is given by

$$\gamma(x'_1 | x_1) = \sum_k n_k \chi_k^{*(1')} \chi_k^{(1)} ,$$

and A(32) gives

$$\gamma(x'_1 | x_1) = \sum_k c_k^2 \chi_k^{*(1)} \chi_k^{(1)} ,$$

omitting the spin functions, for convenience. Comparing these, there evidently exists the relationship that

$$c_k = \pm n_k^{1/2}$$

between the coefficients in the natural expansion A(32) and the occupation numbers, in this two-electron case.

Thus, in this simplified case, there is no need to produce Löwdin's "first-order density in the k-space", the  $\gamma$ -matrix. We can operate instead on the matrix  $\underline{C}$  of the coefficients in the original CI wave-function. NB this is purely a consequence of the fact that the two-electron wave-function may be written as a real quadratic form, A(31), and it is therefore strictly confined to the two-electron case.

If the original set of basis orbitals  $\psi_k$  contains, say, M orbitals, then the wave-function A(30) will contain  $\frac{1}{2}M(M+1)$  terms, if all possible basis orbitals are used to form configurations. The diagonal form A(32), however, will contain only M terms. This enormous simplification cannot be expected in the many-electron case.

Throughout this discussion we have used spin-orbitals, the spatial parts of which may or may not be doubly-filled. If they are doubly-filled, and we have two spin-orbitals for every spatial orbital, we will correspondingly get two natural spin-orbitals for every natural (spatial) orbital. In this case the word "spin" may be dropped from the expression "natural spin-orbital".

(a)

Example on the Two-electron Case:

Consider a simple configuration interaction normalized wave-function:

$$\psi = \frac{1}{\sqrt{2}} \left[ C_1(1s1s) + C_2(1s2s') + C_3(2s'2s') \right]. \quad (i)$$

i.e. we have three configurations whose determinants are composed of normalized Slater-type orbitals.

$$\begin{aligned} C_1 &= 0.23586511 & \eta(s) &= 2.64 \\ C_2 &= 0.37591055 & \eta(s') &= 1.95 \\ C_3 &= 0.17935024 & \int 1s2s' d\tau = S &= 0.71103715 \end{aligned}$$

Writing out (i) in full:

$$\begin{aligned} &= \frac{1}{\sqrt{2}} \left[ C_1 \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} + C_2 \begin{vmatrix} 1s(1)\alpha(1) & 2s'(1)\beta(1) \\ 1s(2)\alpha(2) & 2s'(2)\beta(2) \end{vmatrix} \right. \\ &+ C_2 \begin{vmatrix} 2s'(1)\alpha(1) & 1s(1)\beta(1) \\ 2s'(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} + C_3 \begin{vmatrix} 2s'(1)\alpha(1) & 2s'(1)\beta(1) \\ 2s'(2)\alpha(2) & 2s'(2)\beta(2) \end{vmatrix} \left. \right] \quad (ii) \end{aligned}$$

(a) data for this example is taken from J.D. Stuart and F.A. Matsen, J. Chem. Phys. 41, 1646 (1964). See  $\psi(2)$ , Table II, p. 1647.

Factoring off the spin:

$$\psi = \left[ C_1 1s(1)1s(2) + C_2 1s(1)2s'(2) + C_2 2s'(1)1s(2) + C_3 2s'(1)2s'(2) \right] * \frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \quad (\text{iii})$$

We have four distinct spin-orbitals, but since they are made up from doubly-filled spatial orbitals, we can from now on talk about two natural orbitals. We shall ignore the spin function during this analysis. The spatial orbitals are 1s and 2s', which we shall label ① and ② respectively.

Construction of the  $\underline{\gamma}$ -matrix:

The first-order reduced density matrix is given, from (iii), by

$$\begin{aligned} \gamma(x'_1 | x_1) = & 1s(1)1s(1) (C_1^2 + C_2^2 + 2C_1 C_2 S) \\ & + 1s(1)2s'(1) (C_1 C_2 + C_1 C_3 S + C_2^2 S + C_2 C_3) \\ & + 2s'(1)1s(1) (C_2 C_1 + C_2^2 S + C_3 C_1 S + C_3 C_2) \\ & + 2s'(1)2s'(1) (C_2^2 + C_3^2 + 2C_2 C_3 S) \quad , \quad (\text{iv}) \end{aligned}$$

so we can identify the elements of the  $\underline{\gamma}$ -matrix as

$$\begin{aligned} \gamma(\textcircled{1} | \textcircled{1}) &= C_1^2 + C_2^2 + 2C_1 C_2 S \\ &= 0.32302814 \end{aligned}$$

$$\begin{aligned}\gamma(\textcircled{1}|\textcircled{2}) &= \gamma(\textcircled{2}|\textcircled{1}) = c_1c_2 + c_1c_3s + c_2^2s + c_2c_3 \\ &= 0.28663820\end{aligned}$$

$$\begin{aligned}\gamma(\textcircled{2}|\textcircled{2}) &= c_2^2 + c_3^2 + 2c_2c_3s \\ &= 0.26935098\end{aligned}$$

Thus, the complete  $\underline{\gamma}$ -matrix is

$$\underline{\gamma} = \begin{bmatrix} 0.32302814 & 0.28663820 \\ 0.28663820 & 0.26935098 \end{bmatrix} .$$

The  $\underline{C}$ -matrix will be:

$$\underline{C} = \begin{bmatrix} 0.23586511 & 0.37591055 \\ 0.37591055 & 0.17935024 \end{bmatrix} .$$

The  $\underline{\Delta}$ -matrix will be:

$$\underline{\Delta} = \begin{bmatrix} 1.0 & 0.71103715 \\ 0.71103715 & 1.0 \end{bmatrix} .$$

If we use  $\underline{\Delta}$  and  $\underline{\gamma}$  in the analysis, we get  $\underline{A}$  and  $\underline{n}$  :-

$$\underline{n} = \begin{bmatrix} 0.99759759 & 0 \\ 0 & 0.00240200 \end{bmatrix} \quad \underline{A} = \begin{bmatrix} 0.56542539 & -1.30494943 \\ 0.51552846 & 1.32543469 \end{bmatrix} .$$

(The sum of the occupation numbers is 1 and not 2 because a factor of 2 was omitted from the first-order reduced density matrix, equ. (iv).)

If we use  $\underline{\Delta}$  and  $\underline{C}$  in the analysis, we get  $\underline{A}$  and  $\underline{c}$  :-

$$\underline{c} = \begin{bmatrix} 0.99879829 & 0 \\ 0 & -0.04901019 \end{bmatrix} \quad \underline{A} = \begin{bmatrix} 0.56542538 & -1.30492944 \\ 0.51552847 & 1.32543468 \end{bmatrix} ,$$

and  $c_1 = \sqrt{n_1}$ ,  $c_2 = -\sqrt{n_2}$ . Thus, by two methods, we have the complete natural expansion for  $\Psi$  in (i).