# ELECTRON CORRELATION

## IN THE

 $(1s^{2}2s)^{2}S$  AND  $(1s^{2}2p)^{2}P$  STATES

# OF THE

LITHIUM ISOELECTRONIC SEQUENCE

IN

POSITION AND MOMENTUM SPACE

by

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# ELECTRON CORRELATION IN THE <sup>2</sup>S AND <sup>2</sup>P STATES OF LI-LIKE IONS

#### ABSTRACT

In Part 1, the correlation problem is briefly reviewed and is followed by an outline of some approaches to electron correlation.

In Part 2.1, correlation effects in the ground state of a series of open-shell systems in the form of Li-like ions are examined. The analysis is performed by using a partitioning technique which allows correlation effects in the individual electronic shells to be studied. These effects are examined by means of Coulomb holes, partial holes, various correlation coefficients  $\tau$  and Coulomb several one- and two-particle expectation values. The use of partial Coulomb holes illustrated changes in the relative importance of angular and radial correlation effects as the location of the test electron was varied. Comparisons are made between the K-shell results for the Li-like ions and those for the corresponding shell in some He- and Be-like Similarly, the inter-shell results for Li are ions. compared with their counterparts in both the Be atom and some excited states of He.

In Part 2.2, the study of correlation effects is extended to an examination of the Li-like ions in the  $(1s^22p)^2p$  excited state. These results are compared with those for the ground state, discussed in Part 2.1.

In the light of the results obtained in position space, a parallel investigation of the Li-like ions was carried out in momentum space and those results are presented in Part 3. In momentum space, the contrasting behaviour of the angular and radial components gave insight into the way electron correlation in the K-shell was influenced by the occupation of the L-shell. In addition, the analysis highlighted certain weaknesses in the description of the inter-shells in the excited state wavefunctions. The momentum results for the K-shell are compared for the ground and excited states of Li with Li<sup>+</sup>, Be<sup>2+</sup> and also with the Be results.

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MY FAMILY

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PART ONE

GENERAL INTRODUCTION

# CHAPTER 1.1.1

#### THE CORRELATION PROBLEM

It is well-known that the laws of classical physics are applicable only to the motion of macroscopic particles and not applicable to the discussion of electron motion in atoms and molecules. Consequently the microscopic particle requires a new form of mechanics, termed quantum mechanics (or wave mechanics). The foundations of present day quantum mechanics were laid in 1926 by Schrodinger, who published a series of papers on the subject. In the first of these papers (1), Schrodinger introduced the wave equation which was subsequently extended and successfully applied to a large number of problems. Since then it has become generally accepted that the Schrodinger Wave Equation offers an accurate description of microscopic phenomena. This Wave Equation can be solved exactly for the hydrogen atom and hydrogen molecular ion, each with a single electron. However, for a larger atom or molecule, the problem is made more complicated by the presence of potential energy terms which arise from the mutual repulsion between any two In practice the exact solution to the electrons. Schrodinger equation for a many-electron system is unobtainable. Therefore, in order to make the problem tractable it is necessary to have make use of approximate methods. This is where a knowledge of the physics of the problem becomes important. Any approximations which are made in solving the problem must be physically reasonable if meaningful results are to be obtained. The first and

simplest of such approximations is due to Hartree (2), where we assume that the total wavefunction  $\Psi(1,2,3,\ldots,N)$  for N electrons can be written as a simple product of one-particle wavefunctions:

$$\Psi(1,2,3,\ldots,N) = *_{1}(1)*_{2}(2)*_{3}(3)\ldots*_{N}(N) , \qquad 1.1.1$$

where  $\bullet_i(i)$  depends on the space and spin coordinates of electron i. One of the assumptions in equation (1.1.1) is that the electrons move independently of each other; that is, each electron moves in the average electrostatic potential due to the presence of all the other electrons. One major source of difficulty with the total wavefunction written in the form of equation (1.1.1) is the so-called electron correlation problem. This arises from the fact that the Hartree product function incorrectly describes the electron-electron interactions. To avoid this difficulty and, in particular, to let the Hartree product satisfy the Pauli Exclusion principle and take into account the indistinguishability of electrons, the total wavefunction is written as a single Slater determinant <sup>(3)</sup>,

The component one-particle functions are referred to as spin-orbitals. Any spin-orbital may be written as the

product of a space orbital  $\varphi$  and a spin function  $\alpha$  or  $\beta$ . If  $\Psi$  is determined numerically by an interative self-consistent field procedure, it is called a Hartree-Fock (HF) wavefunction (4-6). Interchanging the coordinates of any two electrons corresponds to interchanging two rows of the Slater determinant, which changes the sign of the determinant. Thus, Slater determinants meet the requirement of the antisymmetry principle. Having two electrons occupying the same spin orbital corresponds to having two columns of the determinant equal, which makes the determinant zero. Consequently, no more than one electron can occupy a given spin orbital (Pauli Exclusion Principle). The HF orbitals are constrained to form an orthonormal set of functions and the multiplying factor  $(N!)^{-1/2}$  ensures that  $\Psi$  is normalized to unity after integration over all the space and spin coordinates for the N-electron system.

The independent-particle wavefunction for an N-particle system, represented at its best from an energy point of view by the Hartree-Fock treatment, allows for some spatial correlation between electrons with parallel spin components by means of the Pauli Exclusion Principle which gives rise to the so-called Fermi-hole (7,8). This causes the Hartree-Fock energy to be lower than the Hartree energy.

In reality, all electrons repel each other due to the Coulomb potential  $e^2/r_{12}$  which exists between them, and each electron is therefore surrounded by a Coulomb hole <sup>(9)</sup> with respect to the other electrons. Within the HF approximat-

ion, the probability of finding two electrons with parallel spins at the same point in space is zero (10, 11). Such a point may be termed the centre of a Fermi hole, and is a consequence of the antisymmetry of the wavefunction. Although the HF method allows electrons with the same spin properties to avoid one another, no allowance is made for any spatial correlation between electrons with opposite spins. The effect of correlation between all electrons can only be examined by means of wavefunctions which are more flexible than the HF determinant. When described by wavefunctions which go beyond the HF level of accuracy, each electron lies in a region of space which is largely devoid of other electrons, this is a consequence of a more realistic description of the Coulombic repulsions. Correlation thus refers to the residual error in the Hartree-Fock model when describing the electron-electron Coulombic interactions.

One may get an idea of the order of the correlation error in the independent particle model by studying the correlation energy (12), which is defined as the difference between the true non-relativistic energy and the HF energy,

$$E_{corr} = E_{exact} - E_{HF}$$
 1.1.3

Since the Hartree-Fock energy is an upper bound to the exact energy the correlation energy is negative. This definition, although straightforward, has the disadvantage of being based on two quantities, neither of which can in principle be known exactly. Gruninger, Ohrn and Lowdin <sup>(13)</sup> have

shown that the major contributions to E<sub>corr</sub> come from the electronic kinetic energy and, in particular, the total electron-electron repulsion energy.

For the ground state (1s)<sup>2</sup> of the He-like ions, the correlation energy is approximately constant -1.1eV, of which amount +1.1eV refers to the kinetic energy and -2.2eV to the potential energy, in accordance with the virial theorem. Similar figures are appropriate for the ground state of the hydrogen molecule, H<sub>2</sub>. It should be observed, however, that the correlation energy per electron pair in general is not a constant and that, for the ground state of atoms, it goes up approximately linearly with increasing atomic number<sup>(14)</sup>. For atoms and small molecules, the correlation energy seems to be approximately one per cent of the total energy. Although this is a relatively small contribution to the total energy it is comparable to spectral transition energies, binding energies and rotational barriers in molecules. For example, the <sup>1</sup>S description of H is particularly sensitive to electron correlation, since without correlation the existence of the ground-state is not even predicted. Many other physical quantities such as absorption frequencies and force constants are directly related to total energies and can therefore be correlation dependent. Energies calculated by the Hartree-Fock method are typically in error by about 1%. On an absolute basis this is not much, but in chemical terms it is still too large. For example, the total energy of the carbon atom is about 1000eV, and 1% of this is 10eV. Chemical bond energies are typically of the order of 100

Kcal/mole, which is 5eV/molecule. Attempting to calculate a bond energy by taking the difference between Hartree-Fock molecular and atomic energies, which are in error by several eV for light atoms, is an unreliable procedure. We must seek a way of improving on Hartree-Fock wavefunctions and energies.

The correlation problem is still a field of active research and many methods of analysing and studying correlation have been proposed. The work of Nesbet<sup>(15)</sup>, Brueckner<sup>(16)</sup> and Sinanoglu<sup>(16)</sup> has been particularly noteworthy. Much of the early work on the problem was due to Hylleraas<sup>(17)</sup> who proposed three methods of constructing a correlated wavefunction, all of which are still in use today.

In the quantum theory of the electronic structure of matter, the two-electron systems provide a valuable bridge between the comparatively simple one-electron systems and systems containing many electrons. The structure of an electronic system within a given nuclear framework depends not only on the balance between the kinetic energy of the electrons and their attraction to the nuclei, but also on mutual electronic repulsion. The last effect causes the considerable difficulties in the theory, since it may not be treated within the conventional one-electron approximat-The accurate solution of the many-electron ion'. Schrodinger equation therefore demands other methods, and the results for two-electron systems are then also of guiding importance in treating systems containing many

electrons. Two types of solution of the two-electron Schrodinger equation have been suggested, namely an eigenfunction in the form of a 'superposition of configurations' and a form containing the interelectronic distance as a variable. Both types were first investigated by Hylleraas in his pioneering work on the helium problem (18). Hylleraas found that the series of configurations converged rather slowly and that a much quicker convergence could be obtained by introducing r<sub>12</sub> explicitly in the solution. Wavefunctions containing r<sub>12</sub> have later been evaluated by James and Coolidge<sup>(19)</sup> for the H<sub>2</sub> molecule, by Henrich<sup>(20)</sup> for the  $H^-$  ion, and for the He series by Eriksson<sup>(21)</sup>, by Baber and Hasse<sup>(22)</sup>, and by Chandrasekhar and Herzberg<sup>(23)</sup>. The wavefunctions containing r<sub>12</sub> have the disadvantage that it seems impossible to give them an interpretation of simple physical visuality, and it is further difficult to generalize the approach to many-electron systems<sup>(24)</sup>. Nevertheless, the success of the r<sub>12</sub> method was so large that, for a rather long time, it was almost generally believed in the literature<sup>(17)</sup> that "electronic correlation" could be taken into account only by introducing the inter-electronic dictances r<sub>ij</sub> explicitly into the wavefunction. However, it was already known in the early days of quantum mechanics that the wavefunction for a many-electron system could be expressed as a superposition of configurations built up from one-electron functions, provided that the one-electron set was complete.

The wavefunctions studied in this work are of the configuration-interaction (CI) $^{(25,26)}$  type and they are

analysed by making use of the many electron theory (MET) proposed by Sinanoglu<sup>(27)</sup>. In the next Chapter, a brief outline is given of some approaches to correlation. In Part 2, we examine the effects of electron correlation using a partitioning technique<sup>(28)</sup> in position space for the ground and first excited states of a series of the Li-like ions. In Part 3, the analysis was performed by determining correlation properties in momentum space by using the Fourier transformation, see Appendix A.3.

# CHAPTER 1.1.2

## THE CALCULATION OF CORRELATION EFFECTS

## (A) Some Approaches to Correlation

The wavefunctions used throughout this work are of the configuration-interaction (CI) type. In this approach, the correlated wavefunction is expanded as a linear combination of Slater determinants<sup>(29)</sup>,

 $\Psi = \Gamma c_{i} \phi_{i} ,$ 

where each of the  $\phi_i$ 's (configurations) is an antisymmetrized product of one-electron functions (spin orbitals), and the coefficients c; are taken as those which minimize the total energy. The exact wavefunction may, in principle, be obtained by applying the variation theorem and solving an infinite set of secular equations. In practice, of course, there is a restriction on the number of configurations that can be conveniently handled; the more terms that can be accommodated, the better the calculated energy. The main drawback of this method is that, at the outset, it is not certain which configurations will be most effective in lowering the energy. In addition it is found that the energy convergence of a CI expansion is notoriously slow. These difficulties can be overcome by expressing the wavefunction in terms of so-called natural spin orbitals (30, 31)(NSO's).

Lowdin<sup>(30)</sup> has defined natural spin orbitals  $Q(\underline{x}_i)$  as being those orbitals which produce a diagonal representation of the first order density matrix  $\Gamma(\underline{x}_1,\underline{x}_1)$ , that is:

$$\Gamma(\underline{x}_{1}, \underline{x}_{1}) = N \int \psi(\underline{x}_{1}, \underline{x}_{2}, \dots, \underline{x}_{N}) \psi^{*}(\underline{x}_{1}, \underline{x}_{2}, \dots, \underline{x}_{N}) d\underline{x}_{2} d\underline{x}_{3} \dots d\underline{x}_{N}$$
$$= \sum_{i} n_{i} Q_{i}(\underline{x}_{1}) Q_{i}^{*}(\underline{x}_{1}) , \qquad 1.1.4$$

where  $\underline{x}_i$  refers to the space and spin coordinates of electron i. The constant  $n_i$  is known as the occupation number of the ith natural orbital (NO) and clearly  $\underline{r}n_i = N$ .

Using a theorem due to Schmidt<sup>(32)</sup> it may be shown that the use of the highest N occupied natural orbitals in a CI wavefunction leads to the most rapidly convergent expansion possible for any basis set of N orbitals. This result may appear to be of little value, since in order to determine the natural orbitals it is first necessary to calculate the density, which in turn requires a knowledge of the exact wavefunction. However, a number of workers have made use of this result by firstly performing an approximate CI calculation, determining approximate natural orbitals and then repeating the procedure but now using only those natural orbitals of highest occupation number and augmenting the basis set with a number of new functions.

The first natural configuration has been found (33,34) to bear a striking resemblance to the Hartree-Fock result in terms of energy and total overlap. The relationship between natural orbitals and Hartree-Fock orbitals has been discussed by several workers (34): for example, Davidson and

Jones<sup>(35)</sup> showed for  $H_2$  that the difference between such orbitals is almost equal to the f function introduced by Sinanoglu<sup>(36)</sup> in the expansion of an N-particle wavefunction. The f functions here represent corrections to the Hartree-Fock orbitals as a consequence of correlation and in general, their contribution to the energy is very small<sup>(37)</sup>.

One approach which has received a great deal of attention in recent years is the Multiconfiguration Self Consistent Field (MCSCF) method. This is a natural bridge between the HF and CI methods. This method was pioneered by Hartree (40) and by Jucys and collaborators (41), and it has been used to calculate the correlation in the ground state atoms<sup>(42)</sup> and molecules<sup>(43)</sup>. The most extensive of application of the MCSCF scheme to excited states, however, has been conducted by Froese<sup>(44,45)</sup>. In this method, the wavefunction is written as a linear combination of Slater determinants, each of which is composed of a set of oneparticle orbitals. However, unlike the CI method these orbitals are not fixed but are to be optimally determined along with the expansion coefficients. The equations determining these orbitals were formulated some years ago by McWeeny<sup>(46)</sup> but their solution has only recently become possible. In practice it is necessary to make a particular choice of the type of configurations to be included in the MCSCF wavefunction. Two different formalisms have been developed - one due to Veillard and Clementi (47) and the other due to Das and Wahl<sup>(48)</sup>. The method developed by the latter is known as the Optimised Valence Configuration (OVC) method. Both of these approaches have been applied to a

number of molecules and although problems remain, particularly with difficulties of convergence, the general MCSCF method seems a promising line of attack for the future.

Some years ago Hurley, Lennard-Jones and Pople<sup>(49)</sup> proposed a method of constructing correlated wavefunctions known as the Separated Pair Approximation. Once again this approximation have generally yielded only about 40-50% of the total correlation energy (calculations on Be and LiH excepted). Furthermore the equations determining the optimum two particle functions are coupled and rapidly become difficult to solve as the number of electrons increase. We shall therefore turn our attention to the Independent Electron Pair Approximations which have been proposed to overcome some of these difficulties.

In Sinanoglu's Many Electron Theory (MET)<sup>(36)</sup> the wavefunction is written, without approximation, in the following form

 $\psi(1,2,\ldots,N) = \phi(1,2,\ldots,N) + X(1,2,\ldots,N) , \qquad 1.1.5$ 

where  $\phi(1,2,\ldots,N)$  and  $\chi(1,2,\ldots,N)$  are, respectively, the HF and correlation functions.  $\phi_{HF}$  is an antisymmetrized product of N spin orbitals

 $\bullet_{\mathrm{HF}}(1,2,\ldots,\mathbf{N}) = \mathbf{A} \bullet_{1}(\underline{\mathbf{X}}_{1}) \bullet_{2}(\underline{\mathbf{X}}_{2}) \ldots \bullet_{\mathbf{N}}(\underline{\mathbf{X}}_{\mathbf{N}})$  1.1.6

and the following orthogonality and normalization

$$\langle \Phi_{\mathrm{HF}} | \times (1, 2, \ldots, N) = 0; \langle \Phi_{\mathrm{HF}} | \Phi_{\mathrm{HF}} \rangle = 1$$

hence  $\langle \phi_{HF} | \psi \rangle = 1$ .

The function X(1,2,...,N) is analyzed into 1,2,...,Nparticle correlation parts by the 'method of successive partial orthogonalization' (MSPO)<sup>(36)</sup>. The detailed form of the correlation part in equation (1.1.5) which one gets from this analysis is

$$X(1,2,...,N) = \sum_{i=1}^{N} \{f_{i}\} + \sum_{i$$

The terms  $\{f_i\}, \{U'_{ij}\}, \dots, \{U'_{12...N}\}$  are the 1, 2, ..., N electron correlation parts where  $\{\}$  indicates antisymmetrization with the products of the remaining (N-n) spin-orbitals, for example

$$\{U'_{ij...n}\} = (n!)^{-1/2} A[(1,2,...,N)U'_{ij...n}/(ij...n]].$$
 1.1.8

The symbolic division by (ij...n) refers to the absence of these orbitals from the HF product (12...N). The n-electron correlation functions have the following orthogonality and antisymmetry properties

$$\int U_{ij\ldots n}^{(\underline{x}_1,\underline{x}_2,\ldots,\underline{x}_N)} \bullet_{\underline{x}}^{(\underline{x}_i)d\underline{x}_i} = 0 , \qquad 1.1.9$$

$$\mathbf{U}_{j,\ldots,n}^{(\mathbf{X}_{1},\mathbf{X}_{j},\ldots,\mathbf{X}_{N})} = -\mathbf{U}_{j,\ldots,n}^{(\mathbf{X}_{j},\mathbf{X}_{1},\ldots,\mathbf{X}_{N})} \qquad 1.1.10$$

where  $\phi_k(\underline{x}_i)$  in equation (1.1.9) is the HF orbital.

The form of equations (1.1.5-10) is general for any  $\Phi_{HF}$ = A(1,2,...,N) in equation (1.1.6) given that these N spinorbitals are orthonormal.

Sinanoglu decomposes the various functions in equation (1.1.7) into a cluster expansion and therefore equation (1.1.7) can be written in the much more detailed form which separates the terms referred to as unlinked clusters and linked clusters. A good approximation to the correlation part in equation (1.1.5) can be written in the following unlinked cluster (16) form:

$$X_{\text{corr}} \approx X_{\text{approx}} = A \left[ (1, 2, ..., N) \{ (2)^{-1/2} \prod_{i < j}^{N} U_{ij} / (ij) + \frac{1/2}{i < j} \sum_{k < 1}^{K} U_{ij} U_{k1} / (ijk1) + ... \} \right] . 1.1.11$$

The above approximation was considered by Levine, Geller and Taylor<sup>(50)</sup> to derive the conditions required for Sinanoglu's wavefunction to describe a singlet state.

So far, the correlation problem reduces to finding the pair correlation functions  $U_{ij}$  which satisfy the orthogonality condition, equation (1.1.9), but are not assumed orthogonal to each other. Substituting equation (1.1.11) into the variational expression for the total energy allows us to determine uncoupled variational equations for each of the pair functions  $U_{ij}$ .

Sinanoglu has suggested that the derivation of pair functions by minimisation of the pair energy functional is similar to the variational problem of solving the helium atom Schrodinger equation. It would seem, therefore, that by using explicitly correlated trial pair functions it should be possible to determine pair energies to the high degree of accuracy that Hylleraas achieved for the energy of the helium atom. Unfortunately, as Geller, Taylor and Levine<sup>(51)</sup> have pointed out, the presence of the Coulomb exchange operators in the expression for the pair energy makes the inclusion of the interelectronic separation  $r_{12}$  in the trial pair function more difficult to handle than in the calculation of an approximate helium wavefunction.

Hurley, Lennard-Jones, and Pople<sup>(49)</sup> proposed the use of a variational trial function

$$\Psi = \det \psi_{12}(1,2)\psi_{34}(3,4) \dots \psi_{N-1,N}(N-1,N) \qquad 1.1.12$$

where det symbolizes the total antisymmetrizing operator, multiplied by a normalization constant. The two-particle wavefunctions  $\psi_{ij}$ , called geminals in the more recent literature, describe localized pairs of electrons. The geminal functions themselves correspond to chemical ideas of molecular structure based on inner shells, valence bonds, and lone pairs of electrons.

The paired-electron wavefunction, equation (1.1.12), has the advantage of descibing what is expected to be the dominant effect of electronic correlation, modification of

pairs of doubly occupied localized orbitals. This is accomplished with a wavefunction adapted to direct variational calculations.

The obvious disadvantage of the paired-electron wavefunction is that it makes no provision for correlation between different localized electron pairs.

It was originally proposed by  $Brueckner^{(52,53)}$ , in the context of a study of nuclear matter, that the correlation problem could be solved independently for each pair of particles in a many-particle system. The proposal by Sinanoglu<sup>(16)</sup> for the solution of the exact pair equations, is closely related to the method of Brueckner, Bethe, and Goldstone. The calculations of Geller, Taylor and Levine on the Be  $atom^{(51)}$ , based on Sinanoglu's formalism, are in fact a variational solution of the Bethe-Goldstone equations, using trial functions that depend explicitly on relative coordinates. The Bethe-Goldstone equation for pair (ij) can be expressed in a variational formalism involving N-particle wavefunctions<sup>(54)</sup>. Nesbet showed the Bethe-Goldstone<sup>(55)</sup> equation, whose solution describes the correlation of electron pair (ij), to be exactly equivalent to a variational determination of the coefficients  $c_{ij}^{ab}$  in a total wavefunction of the form:

$$\Psi_{ij}(\underline{X}_1, \dots, \underline{X}_N) = \phi_0 + \Sigma \phi_{ij}^{ab} \phi_{ij}^{ab}, \qquad 1.1.13$$

for which the occupied orbitals in  $\phi_0$  are Brueckner orbitals. Nesbet then extended this method by proposing that an mth order-Goldstone equation may be defined whose

solution is equivalent to a variational calculation using a trial wavefunction  $\Psi_{ijk...}$  which is a linear combination of  $\phi_o$  and all Slater determinants  $\phi_{ijk...}^{abc...}$  where the indices ijk... may be any subset of the original list i,j,k,l, etc. A comparison of the Nesbet-Bethe-Goldstone approach to second order with Sinanoglu's approach shows that neglect of the orbital correction function  $f_i$  is equivalent to a neglect of the single excitations in Nesbet's method, while the assumption that the electron pair may be treated as uncoupled is equivalent to Nesbet's use of a separate variational equation for each pair. Similar approaches to the Sinanoglu and Nesbet methods of determination of pair correlation functions have been proposed by Szasc<sup>(56)</sup>, Byron and Joachain<sup>(57)</sup>, Krauss and Weiss<sup>(58)</sup> and many others.

# (B) Determination of $f_i$ and $U_{ij}$ within the Many Electron Theory of Sinanoglu

To determine an  $f_i$  correction function we use the method of successive partial orthogonalizations (MSPO)<sup>(36)</sup>. Equation (1.1.5) is multiplied by the orbital product  $\Pi_i$ , which represents the product of all occupied HF spin orbitals except  $\phi_i(i)$ , and then we integrate the result over all coordinates occuring in  $\Pi_i$ . Thus we obtain a function of  $\chi_i$  only, namely,

$$\langle \Psi_{corr} | \Pi_{i}(i) \rangle = N \left[ \Phi_{i}(\underline{x}_{i}) + f_{i}(\underline{x}_{i}) \right] .$$
 1.1.14

The constant N in equation (1.1.14) arises from the normalizing constant implicit in the antisymmetrizer operator A.

To evaluate N, we multiply equation (1.1.5) by the product of all occupied HF spin orbitals  $\Pi$  and integrate over all coordinates,

$$N = \langle \Psi_{corr} | \Pi \rangle_{all} \qquad 1.1.15$$

Substituting equation (1.1.15) into (1.1.14) we get

$$f_{i}(\underline{x}_{i}) = \langle \Psi_{corr} | \pi_{i} \rangle_{\underline{x}_{i}} / \langle \Psi_{corr} | \pi \rangle_{all} - \phi_{i}(\underline{x}_{i}) \quad . \qquad 1.1.16$$

By means of a similar process we may obtain explicit formulae for the pair functions. Thus, multiplication of equation (1.1.5) by  $\Pi_{ij}$ , which is equivalent to  $\Pi$  but with the omission of the orbitals  $\phi_i(\underline{x}_i)$  and  $\phi_j(\underline{x}_j)$ , yields, after integration over all the space-spin coordinates occurring in  $\Pi_{ij}$ ,

$$\langle \Psi_{corr} | \Pi_{ij} \rangle = N[ \Phi_{i}(\underline{x}_{i}) \Phi_{j}(\underline{x}_{j}) - \Phi_{i}(\underline{x}_{j}) \Phi_{j}(\underline{x}_{i}) \\ + \Phi_{i}(\underline{x}_{i}) \Phi_{j}(\underline{x}_{j}) - \Phi_{i}(\underline{x}_{j}) \Phi_{j}(\underline{x}_{i}) \\ + \Phi_{i}(\underline{x}_{i}) \Phi_{j}(\underline{x}_{j}) - \Phi_{i}(\underline{x}_{j}) \Phi_{j}(\underline{x}_{i}) \\ + \sqrt{2} U_{ij}(\underline{x}_{i}, \underline{x}_{j}) ] .$$
 1.1.17

Substitution of N from equation (1.1.15) gives the following relationship for the pair function  $U_{ij}(\underline{x}_i, \underline{x}_j)$ :

$$\begin{aligned} U_{ij}(\underline{x}_{i},\underline{x}_{j}) &= 1/\sqrt{2} \left[ \langle \Psi_{corr} | \Pi_{ij} \rangle / \langle \Psi_{corr} | \Pi \rangle \\ &- \phi_{i}(\underline{x}_{i}) \phi_{j}(\underline{x}_{j}) + \phi_{i}(\underline{x}_{j}) \phi_{j}(\underline{x}_{i}) \\ &- f_{i}(\underline{x}_{i}) \phi_{j}(\underline{x}_{j}) + f_{i}(\underline{x}_{j}) \phi_{j}(\underline{x}_{i}) \\ &- \phi_{i}(\underline{x}_{i}) f_{j}(\underline{x}_{j}) + \phi_{i}(\underline{x}_{j}) f_{j}(\underline{x}_{i}) \right] . \quad 1.1.18 \end{aligned}$$

It is clear that this process may be extended to obtain explicit expressions for any of the higher multielectron correlation terms such as U<sub>ijk</sub>, U<sub>ijkl</sub>, etc.

By the above procedure, we may separate the correlation effects due to intershell or intrashell pair interactions. For the exact wavefunction it is easy to show that the total correlation energy  $E_{corr}$  may be represented by the sum of the pair correlation energies  $\varepsilon_{ij}$  defined by

$$\varepsilon_{ij} = \langle \phi_i \phi_j | r_{ij}^{-1} | U_{ij} \rangle , \qquad 1.1.19$$

where  $U_{ij}$  is given by equation (1.1.18). Banyard and Taylor<sup>(65)</sup> evaluated the pair correlation function  $U_{ij}$  and their associated energies  $\varepsilon_{ij}$  for the He(<sup>1</sup>S)-, Li(<sup>2</sup>S and <sup>2</sup>P)- and Be(<sup>1</sup>S)-like ions.

In this survey, coupled with the previous chapter, we have outlined many of the methods which have been used in the field of atomic and molecular structure calculations. As we have seen, most of these methods are essentially extensions of either the self-consistent field approximation, the configuration interaction method or of the use of explicitly correlated wavefunctions.

PART TWO

ELECTRON CORRELATION IN LI-LIKE IONS IN POSITION SPACE

2.1 GROUND STATE -  $(1s^22s)^2s$ 

2.2 EXCITED STATE -  $(1s^22p)^2p$ 

2.1 GROUND STATE -  $(1s^22s)^2s$ 

.

# CHAPTER 2.1.1

## INTRODUCTION

Here we concern ourselves with a study of electron correlation in position space. In particular, we employ the concept of the Coulomb hole, which has been used extensively to examine the ground state of both He-like ions<sup>(60)</sup> and Belike ions<sup>(28)</sup> in position space. With regard to the heliumlike ions, detailed discussions have been presented of the Coulomb hole in position space for both the ground state and some excited states<sup>(61)</sup>. An obvious and interesting extension of this work would be to examine the Li-like ions, since they represent the simplest systems with an open-shell structure.

The electron-electron distribution function  $f(r_{12})$ , which describes the probability of locating two electrons separated by the interelectronic distance  $r_{12}$ , was first introduced by Coulson and Neilson<sup>(63)</sup> in their study of electron correlation in the 1<sup>1</sup>S ground state of He. The Coulomb hole was then defined as

$$\Delta f(r_{12}) = f_{corr}(r_{12}) - f_{HF}(r_{12}) \qquad 2.1.1$$

where each  $f(r_{12})$  is normalized to unity, and  $f_{corr}(r_{12})$  is the distribution function for  $r_{12}$  evaluated from the correlated wavefunction, and  $f_{HF}(r_{12})$  is derived from the best uncorrelated wavefunction, that is, the Hartree-Fock wavefunction. This definition of the Coulomb hole is entirely analogous to that for the correlation energy<sup>(12)</sup>

and is applicable to all atoms and molecules containing two or more electrons. To make some examination of the way in which the inter-particle distribution function changes for specific locations of one of the electrons, say a test electron 1, we may consider a related distribution function  $g(r_{12},r_1)$ , introduced initially by Boyd and Coulson<sup>(64)</sup>. Changes in this function as a consequence of introducing electron correlation into the wavefunction are clearly of interest.

Recently, Banyard and co-workers (28,65) have used the many electron theory (MET) of Sinanoglu<sup>(36)</sup> to examine electron correlation effects in some detail for the ground state of Be<sup>(65)</sup> and several Be-like ions<sup>(28)</sup>. In an endeavour to gain insight into correlation effects for specific electronic shells within an N-electron system, these workers used the Sinanoglu expansion of the wavefunction to partition the correlated two-particle density which is required for the evaluation of correlation properties in individual normalized electronic shells within the system. Correlation effects for each electronic shell were then assessed with respect to the corresponding restricted Hartree-Fock (RHF) description by evaluating the Coulomb hole, the partial Coulomb holes and the changes which occur in the one- and two-particle radial density distributions. For the intra-shell, it was also of interest determine various radial and angular statistical to correlation coefficients  $\tau$ .

In the present work we extend the analysis to a series of open-shell systems by considering several Li-like ions in the ground state. These three-electron systems, with the electronic configuration  $(1s^22s)^2S$ , represent the simplest ground state example in which both Coulomb correlation and Fermi correlation are present. Coulomb correlation operates between any pair of electrons and is particularly pertinent when the electrons possess antiparallel spin components and are described by a closed-shell, such as, for example, (1s)<sup>2</sup>. Fermi correlation arises between electrons which possess parallel spin components. In addition, the imbalance between the  $\alpha$ - and  $\beta$ -spins of the electrons in the ground-state of the Li-like ions produces a polarization effect in the K-shell. Following the procedure used for the Be-like ions, the two-particle density was partitioned into its pair-wise components and the correlation effects were examined, as before<sup>(28)</sup>, in terms of Coulomb holes, statistical correlation coefficients and several expectation values. The correlation effects in the KaK<sub>β</sub>-shell are compared with those for the doubly-occupied K-shells of the Heand Be-like series of ions, the KaLa and KBLa inter-shells effects are contrasted with the corresponding shells in the Be-like ions and, further, some comparison can be made with the correlation-induced changes in the 2'S and  $2^{3}$ S excited-states of He<sup>(66)</sup>.

Note that, during the course of this work, it was reconfirmed that the correlated wavefunction of Weiss<sup>(25)</sup> for the <sup>2</sup>S-state of the C<sup>3+</sup> ion contains an error. Consequently this function has not been used.

# CHAPTER 2.1.2

## WAVEFUNCTIONS AND ANALYSIS

Using the method of configuration interaction (CI), Weiss<sup>(25)</sup> represented the correlated description of the  $(1s^22s)^2S$  state of the Li-like ions, for  $3 \le Z \le 8$ , as a linear combination of many-electron functions

$$\Psi_{CI}(123) = \Gamma_{i} c_{i} \phi_{i}(123) , \qquad 2.1.2$$

where the coefficients  $c_i$  are taken as those which minimize the total energy and each configuration  $*_i$  is an antisymmetrized product of one-electron functions (spin orbitals).

Two general types of linearly independent configuration were constructed for the three-electron systems. The first of these corresponds to the situation where two electrons couple together to produce singlet S symmetry, and the resulting pair is then coupled with the orbital description of the third electron to produce the overall  $^2$ S symmetry of the state. In the second case, the two electrons are coupled to produce triplet S symmetry, and the resulting pair is again coupled with the third electron to produce a doublet S state ( $^2$ S). These configurations have the form:

$$\Phi_{pqk,\lambda} = (x_{p}x_{q})^{1}Sx_{k}$$

$$= (6D_{\lambda})^{-1/2} \sum_{\substack{\mu=-\lambda}}^{+\lambda} [X^{\mu}_{p\lambda}\alpha(1)\overline{x}^{\mu}_{q\lambda}\beta(2)x_{k}\alpha(3)]$$

$$- [\overline{x}^{\mu}_{p\lambda}\beta(1)x^{\mu}_{q\lambda}\alpha(2)x_{k}\alpha(3)] = 2.1.3$$

and

$$\begin{vmatrix} x^{\mu}_{p\lambda} \alpha(1) & x^{\mu}_{q\lambda} \beta(1) & x_{k} \alpha(1) \\ | & | \\ | & | \\ | & x^{\mu}_{p\lambda} \alpha(2) & x^{\mu}_{q\lambda} \beta(2) & x_{k} \alpha(2) \\ | & | \\ | & | \\ | & x^{\mu}_{p\lambda} \alpha(3) & x^{\mu}_{q\lambda} \beta(3) & x_{k} \alpha(3) \end{vmatrix}$$

The basis set {X} consists of non-orthogonal Slater type orbitals (STO's)

$$\times_{nlm}(r\theta\phi;\xi) = [(2\xi)^{2n+1}/(2n!)]^{1/2} r^{n-1} e^{-\xi r} \Psi_{l,m}(\theta,\phi), 2.1.6$$

where each function X has been normalized to unity. The  $\alpha$ and  $\beta$  spin functions represent the two components of spin. The sum over the azimuthal quantum index  $\mu$  from  $-\lambda$  to  $+\lambda$  in equations (2.1.3) and (2.1.4) ensures that the electron pair forms either <sup>1</sup>S or <sup>3</sup>S symmetry, respectively. The orbital angular momentum index  $\lambda$  specifies the symmetry of the space orbital  $\chi_{nlm}(r \theta \phi; \xi)$  and  $D_{\lambda}$  designates its degeneracy. The bar over the spin-orbitals represents the complex conjugate, with the phase of the spherical harmonic chosen such that  $\bar{\Upsilon}^{\mu}_{\lambda}(\theta,\phi) \ = \ \Upsilon^{-\mu}_{\ \lambda}(\theta,\phi) \quad . \label{eq:gamma-star}$ 

Although these CI wavefunctions of Weiss were determined several years ago, they still rate amongst the energetically best functions since, besides their compactness, they do account for over 97.8%, 97.3%, 97.7%, 96.2%, 95.6% and 94.9% of the correlation energy for Z = 3,4,5,6,7 and 8, respectively. The percentage correlation energy obtained in the CI calculations is defined as

$$E_{corr} = 100 (E_{corr} - E_{HF}) / (E_{exp} - E_{HF}) ,$$

where  $E_{corr}$  is the energy of the CI wavefunction,  $E_{exp}$  is the experimental energy used above and  $E_{HF}$  is the energy of wavefunction. Each wavefunction contains 45 the HF configurations formed from 20 basis orbitals, seven of s type symmetry (1s,1s',1s",2s,2s',2s",3s'), six of p (2p,2p',2p", 3p,3p',3p"), four of d (3d,3d',4d,5d), two of f (4f,5f), and one of g type (5g). The primes associated with orbitals of the same quantum number 1 indicate a different orbital exponent (g). The STO exponents for the K-shell basis functions were identical to these obtained by Weiss<sup>(25)</sup> from a 35-term CI study of the 1<sup>1</sup>S state of the appropriate He-like ions. For each three-electron ion, the exponents of the basis functions for the outer shell were optimized, along with all the CI coefficients, by means of the energy variation method.

The uncorrelated reference state, also determined by Weiss, was represented by a restricted HF wavefunction<sup>(26)</sup>

which, for the ground-state of the Li-like ions, can be written as a single determinant of one-electron functions, namely

$$\bullet_{\rm HF}(123) = (3!)^{-1/2} | \varphi_{1s}^{\alpha}(1) \varphi_{1s}^{\beta}(2) \varphi_{2s}^{\alpha}(3) | . 2.1.7$$

The function  $\varphi_{nlm}(r \theta \phi; \xi)$  is the spatial part of the spinorbital and was constructed from a basis set of six s-type orbitals,

$$\varphi_{nl} = \sum_{i=1}^{6} c_n^i \times \frac{i}{nl} \qquad 2.1.8$$

The basis functions employed here were standard normalized STO's and they are defined as in equation (2.1.6). For a given system, Weiss minimized the total energy with respect to all parameters, including the orbital exponents.

By analogy with the definition of the correlation energy<sup>(12)</sup>, the correlation effects are measured relative to the corresponding Hartree-Fock properties. The examination of correlation properties such as Coulomb holes, one- and two-particle expectation values, etc., requires the evaluation of the two-particle density for both the HF and correlated wavefunctions. When considering the correlated description we adopt the procedure of Sinanoglu<sup>(36)</sup> mentioned in Chapter 1.1.2, and the correlated wavefunction for a three-electron system can be written as

$$\Psi_{\rm corr}(123) = \Phi_{\rm HF}(123) + X_{\rm corr}(123),$$
 2.1.9

where the leading term  $\bullet_{\rm HF}$  in equation (2.1.9) is chosen to be the restricted HF wavefunction. Since this reference state is a single determinant, it can be expressed as the antisymmetrized product of all occupied HF spin-orbitals

$$\bullet_{\rm HF}(123) = A \Pi(123)$$
 2.1.10

where

$$\pi(123) = *_1(\underline{x}_1) *_2(\underline{x}_2) *_3(\underline{x}_3) , \qquad 2.1.11$$

unless stated otherwise, A is the 3-electron antisymmetrizer given by

$$A = (3!)^{-1/2} \sum_{p} \sum_{p} P \qquad 2.1.12$$

and P is the permutation operator and  $\varepsilon_p$  takes the values +1 and -1 for even and odd permutations, respectively. The HF spin orbitals  $\blacklozenge$  are designated by the numerals 1,2,3 starting with the lowest orbital with spin  $\alpha$ , consequently all odd integers are for  $\alpha$  spin and all even ones for  $\beta$ spin. Before the antisymmetrizer is applied in equation (2.1.10), spin orbital i is occupied by electron i whose space-spin coordinates are represented by  $x_i$ .

The correlation part X in equation (2.1.9) can be written as

$$N=3 N=3 N=3 N=3$$

$$X(123) = \Sigma X_{i} + \Sigma X_{ij} + \Sigma X_{ijk} 2.1.13$$

$$i=1 i < j i < j < k$$
where

$$Xi = A\{\Pi(123) f_{i}/(i)\},$$
 2.1.14

$$X_{ij} = (2)^{-1/2} A(\pi(123) U_{ij}/\phi_i\phi_j)$$
, 2.1.15

and

$$X_{ijk} = (3!)^{-1/2} A\{ \pi(123) U_{ijk} / \phi_i \phi_j \phi_i \} . 2.1.16$$

The function f<sub>i</sub> is the orbital correction term corresponding to the ith normalized spin orbital  $\phi_i$ ,  $U_{ij}$  is the paircorrelation function associated with  $\phi_i$  and  $\phi_j$ , and  $U_{ijk}$  is the higher many-electron correlation term. In equations (2.1.14 - 16), we have used the convention

$$f_{i}/\phi_{i} = f_{i}(\underline{x}_{i})/\phi_{i}(\underline{x}_{i})$$
$$U_{ij}/\phi_{i}\phi_{j} = U_{ij}(\underline{x}_{i},\underline{x}_{j})/\phi_{i}(\underline{x}_{i})\phi_{j}(\underline{x}_{j}) , \text{etc.}$$

Expressions for  $f_i$  and  $U_{ij}$  were obtained by the method of successive partial orthogonalizations (MSPO) proposed by Sinanoglu<sup>(36)</sup>. The correlation terms U are antisymmetric under an odd number of permutations, i.e.:

$$U_{ij}(\underline{x}_{i},\underline{x}_{j}) = U_{ij}(i,j) = -U_{ij}(\underline{x}_{j},\underline{x}_{i}) , \qquad 2.1.17$$

$$U_{ij}(\underline{x}_{i},\underline{x}_{i}) = -U_{ij}(\underline{x}_{i},\underline{x}_{i}) , \qquad 2.1.18$$

$$U_{ijk}(\underline{x}_{i},\underline{x}_{j},\underline{x}_{k}) = -U_{ijk}(\underline{x}_{j},\underline{x}_{i},\underline{x}_{k}) \qquad 2.1.18$$

The correlation function X(123) in equation (2.1.9) is orthogonal to all the occupied spin-orbitals in  $\phi_{\rm HF}$  since the MSPO procedure is based on the following requirements:

$$\langle f_{i} | \phi_{1} \rangle = 0$$
  
 $\langle U_{ij} | \phi_{1} \rangle = 0$  (1=1,2,3) 2.1.19  
 $\langle U_{ijk} | \phi_{1} \rangle = 0$  ,

where

Let us now consider each component of the correlated wavefunction in more detail. The first term in  $\Psi_{corr}(123)$ given in equation (2,1,9) is the RHF function  $\bullet_{\rm HF}(123)$ . This may be expanded in terms of its normalized spinorbitals  $\bullet_i$  as follows:

$$\Phi_{\rm HF}(123) = (N!)^{-1/2} \sum_{\substack{(i < j) \neq k}}^{N=3} A_{ij}^{12} \Phi_{k}(3) \varepsilon_{p} \qquad 2.1.23$$

where, for convenience, we have introduced the abbreviated notation

$$A_{ij}^{12} = *_{i}(\underline{x}_{1}) *_{j}(\underline{x}_{2}) - *_{j}(\underline{x}_{1}) *_{i}(\underline{x}_{2}) . \qquad 2.1.24$$

Turning now to the correlated part of equation (2.1.9), we see from equation (2.1.13) that X(123) consists of three contributions. The first part, involving the orbital correction function  $f_i$ , is written as

N=3  

$$\Sigma \times_{i} = A [\pi(123) \{ f_{1}/ *_{1} + f_{2}/ *_{2} + f_{3}/ *_{3} \}] 2.1.25$$
  
i

$$= \mathbf{A} \{ \mathbf{f}_{1} \mathbf{*}_{2} \mathbf{*}_{3} + \mathbf{*}_{1} \mathbf{f}_{2} \mathbf{*}_{3} + \mathbf{*}_{1} \mathbf{*}_{2} \mathbf{f}_{3} \} . \qquad 2.1.26$$

Each term in the above equation can be expanded after applying the antisymmetrizer to give

$$\sum_{i}^{N=3} X_{i} = \frac{1}{(N!)^{-1/2}} \left[ \left\{ f_{1}(x_{1}) + g_{2}(x_{2}) - f_{2}(x_{1}) f_{1}(x_{2}) + g_{3}(x_{3}) - \left( f_{1}(x_{1}) + g_{3}(x_{2}) - f_{3}(x_{1}) f_{1}(x_{2}) + g_{2}(x_{3}) + \left( f_{2}(x_{1}) + g_{3}(x_{2}) - f_{3}(x_{1}) + g_{2}(x_{2}) + f_{1}(x_{3}) + \left( f_{1}(x_{1}) f_{2}(x_{2}) - f_{2}(x_{1}) + f_{1}(x_{2}) + g_{3}(x_{3}) - \left( f_{1}(x_{1}) + g_{3}(x_{2}) - f_{3}(x_{1}) + f_{1}(x_{2}) + f_{2}(x_{3}) + \left( f_{2}(x_{1}) + g_{3}(x_{2}) - f_{3}(x_{1}) + f_{2}(x_{2}) + f_{1}(x_{3}) + \left( f_{2}(x_{1}) + g_{3}(x_{2}) - f_{3}(x_{1}) + f_{2}(x_{2}) + f_{3}(x_{3}) - \left( f_{1}(x_{1}) + g_{2}(x_{2}) - f_{3}(x_{1}) + f_{1}(x_{2}) + f_{3}(x_{3}) + \left( f_{2}(x_{1}) + g_{3}(x_{2}) - f_{3}(x_{1}) + f_{1}(x_{2}) + g_{2}(x_{3}) + \left( f_{2}(x_{1}) + g_{3}(x_{2}) - f_{3}(x_{1}) + f_{1}(x_{2}) + g_{2}(x_{3}) + \left( f_{2}(x_{1}) + g_{3}(x_{2}) - f_{3}(x_{1}) + f_{1}(x_{2}) + g_{2}(x_{3}) + \left( f_{2}(x_{1}) + g_{3}(x_{2}) - f_{3}(x_{1}) + g_{2}(x_{2}) + f_{1}(x_{3}) \right] - 2.1.27$$

Thus, the final form of 
$$\sum_{i}^{N=3} X_{i}$$
 may be expressed as  

$$\sum_{i}^{N=3} \sum_{i}^{N=3} X_{i} = (N!)^{-1/2} \sum_{\substack{i \\ (i < j) \neq k}} [A_{ij}^{12}f_{k}(3) + (B_{ij}^{12} + D_{ij}^{12}) + (A_{ij}^{12} + D_{ij}^{12}) +$$

where

$$B_{ij}^{12} = \phi_{i}(x_{1})f_{j}(x_{2}) - f_{j}(x_{1})\phi_{i}(x_{2}) \qquad 2.1.29$$

and

$$D_{ij}^{12} = f_{i}(x_{1}) *_{j}(x_{2}) - *_{j}(x_{1}) f_{i}(x_{2}) . \qquad 2.1.30$$

The second correlation part of X(123) involves the paircorrelation functions  $U_{ij}$ . This contribution may be rewritten, using the same procedure as before, to give

$$\sum_{i < j}^{N=3} x_{ij} = (2!)^{-1/2} A[\pi(123) \{ U_{12}/_{1}^{\phi} + U_{23}/_{2}^{\phi} + U_{13}/_{1}^{\phi} + U_{23}/_{2}^{\phi} + U_{23}/_{2}^{\phi}$$

The superscripts on the pair-functions U<sub>ij</sub> refer to the electron coordinates. The use of the antisymmetrizer A then gives

$$\sum_{i < j}^{N=3} X_{ij} = (2!3!)^{-1/2}$$

$$\left[ \{ U_{12}^{12} - U_{12}^{21} \} \diamond_{3}(3) + \{ U_{13}^{21} - U_{13}^{12} \} \diamond_{2}(3) + \{ U_{23}^{12} - U_{23}^{21} \} \diamond_{1}(3) + \{ U_{12}^{31} - U_{12}^{13} \} \diamond_{3}(2) + \{ U_{12}^{23} - U_{12}^{32} \} \diamond_{3}(1) + \{ U_{13}^{13} - U_{13}^{31} \} \diamond_{2}(2) + \{ U_{13}^{32} - U_{13}^{22} \} \diamond_{3}(1) + \{ U_{23}^{23} - U_{23}^{32} \} \diamond_{1}(1) + \{ U_{23}^{23} - U_{23}^{22} \} \diamond_{1}(1) + \{ U_{23}^{31} - U_{13}^{13} \} \diamond_{1}(2) \right] \qquad 2.1.33$$

Equation (2.1.33) may now be represented in the compact form

$$\sum_{i < j}^{N=3} \sum_{\substack{i < j}} x_{ij} = (2!/3!)^{1/2} \sum_{\substack{(i < j) \neq k}}^{N=3} \varepsilon_p \{ U_{ij}^{12} \phi_k(3) + U_{ij}^{23} \phi_k(1) + U_{ij}^{31} \phi_k(2) \} .$$
 2.1.34

For N=3, the last correlation part of equation (2.1.13) reduces to  $X_{123}$  and contains only the one three-electron function U<sub>123</sub>. Thus, equation (2.1.16) becomes

$$X_{123} = (3!)^{-1/2} AU_{123} = (2/3!)$$
  
 $\sum_{\substack{(i < j) \neq k}}^{N=3} U_{ijk} \varepsilon_{p}$ . 2.1.35

Substituting equations (2.1.28), (2.1.34) and (2.1.35) into equation (2.1.13), we get

$$X(123) = (N!)^{-1/2} \sum_{\substack{i < j \\ j \neq k}}^{N=3} \sum_{\substack{i < j \\ j \neq k}} [[A_{ij}^{12}f_{k}(3) + \{B_{ij}^{12} + D_{ij}^{12}\} + k(3)] + \sqrt{2} \{ U_{ij}^{12} + U_{ij}^{23} + U_{ij}^{23} + k(1) + U_{ij}^{31} + k(2) + \sqrt{2} \{ U_{ijk}^{12} + U_{ijk}^{23} + k(1) + U_{ijk}^{31} + k(2) + \sqrt{2} \}]. 2.1.36$$

The above expression is the correlated part of the total wavefunction (see equation (2.1.9)), written in terms of its basic components.

## CHAPTER 2.1.3

## CALCULATIONS AND RESULTS

For an N-electron system, the change in the two-particle density due to electron correlation can be written as

$$\Delta\Gamma(\underline{x}_{m},\underline{x}_{n}) = \Gamma_{corr}(\underline{x}_{m},\underline{x}_{n}) - \Gamma_{HF}(\underline{x}_{m},\underline{x}_{n}) \quad . \quad 2.1.37$$

The definition of  $\Gamma(\underline{x}_m, \underline{x}_n)$  in terms of an N-particle wavefunction follows, for example, McWeeny and Sutcliffe<sup>(67)</sup>. Thus,

$$\Gamma(\underline{x}_{\underline{m}},\underline{x}_{\underline{n}}) = \binom{N}{2} \int \Psi^{*}(\underline{x}_{1},\underline{x}_{2},\dots,\underline{x}_{N}) \Psi(\underline{x}_{1},\underline{x}_{2},\dots,\underline{x}_{N})$$
$$d\underline{x}_{\underline{p}},\dots,d\underline{x}_{N} \qquad 2.1.38$$

where  $\underline{x}_{m}$  and  $\underline{x}_{n}$  are the space spin co-ordinates of any two electrons m and n, and  $d\underline{x}_{p}, \dots d\underline{x}_{N}$  indicates integrationsummation over the combined space and spin co-ordinates of all N-electrons except m and n. The binomial coefficient  $\binom{N}{2}$ , which can be written as

$$\binom{N}{2} = N! / [2!(N-2)!] , 2.1.39$$

ensures that the two-particle density  $\Gamma(\underline{x}_m, \underline{x}_n)$  is normalized to the number of independent electron pairs within the system, so that

$$\int \Gamma(\underline{\mathbf{x}}_{\mathbf{m}}, \underline{\mathbf{x}}_{\mathbf{n}}) d\underline{\mathbf{x}}_{\mathbf{m}} d\underline{\mathbf{x}}_{\mathbf{n}} = \binom{\mathbf{N}}{2} \quad . \qquad 2.1.40$$

Correlation effects can be examined within the individual

electronic shells by partitioning each  $\Gamma(\underline{x}_{m}, \underline{x}_{n})$  into its pair-wise components (i,j), where (i,j) labels the occupied normalized spin-orbitals  $\bullet_{i}$  and  $\bullet_{j}$  in the restricted HF representation. The partitioning of the restricted HF twoparticle density into its KaK $\beta$ -, KaLa- and K $\beta$ La-components is both straightforward and exact. For the Li-like ions, the substitution of equation (2.1.23) into equation (2.1.38), followed by integration over the space and spin coordinates of one of the electrons, yields

$$\Gamma_{\rm HF}(\underline{x}_{\rm m},\underline{x}_{\rm n}) = 1/2 \sum_{\substack{i < j \\ i < j}}^{N=3} A_{ij}^2$$
, 2.1.41

where  $A_{ij}$ , is defined as in equation (2.1.24); see also Appendix A.1. The partitioning of  $\Gamma_{corr}(\underline{x}_m, \underline{x}_n)$  into its intra- and inter-shell components is, of necessity, only approximate and follows the procedure adopted by Banyard and Mashat<sup>(28)</sup>. The Sinanoglu representation of the correlated wavefunction was substituted into equation (2.1.38) and, as outlined in the earlier work<sup>(28)</sup>, we omitted contributions to  $\Gamma_{corr}(\underline{x}_m, \underline{x}_n)$  arising from  $X^*(123)X(123)$ . Thus, in equation (2.1.38),  $\Psi_{corr}^*(123)\Psi_{corr}(123)$  is approximated by

$$\Psi_{corr}^{*}(123)\Psi_{corr}^{*}(123) \approx c^{2} \{ \phi_{HF}^{*}(123) \phi_{HF}^{*}(123) + \phi_{HF}^{*}(123) \}$$

$$*_{\rm HF}^{*}(123)\times(123) + *_{\rm HF}^{*}(123)\times(123)$$
, 2.1.42

where the constant c ensures normalization. As shown in Appendix A.1, the evaluation of the correlated two-particle density requires integration over the space and spin coordinates of, say, electron 3 and, consequently, this

removes the  $U_{123}$  term which occurs within X(123). Thus, we obtain a partitionable two-particle density of the form

$$\Gamma_{\rm corr}(\underline{x}_1, \underline{x}_2) = \sum_{i < j}^{N=3} A_{ij}^{12} \{ \langle \Psi_{\rm corr} | \Pi_{ij} \rangle / \langle \Psi_{\rm corr} | \Pi \rangle - \frac{1}{2} A_{ij}^{12} \}, \quad 2.1.43$$

where, for convenience, we have now chosen m and n to be 1 and 2, respectively. The density for each pair (i,j) is normalized to unity. The symbol T represents the product of all occupied HF spin-orbitals and similarly for  $\pi_{ij}$  but with the omission of the spin-orbitals  $\bullet_i$  and  $\bullet_j$ . This approximate representation of the correlated two-particle density was then used in conjunction with the HF description in order to determine Coulomb holes and expectation values for each shell.

Within the above approximation, the change in the twoparticle density,  $\Delta\Gamma(\underline{X}_1,\underline{X}_2)$ , due to electron correlation, can be written as

$$\Delta\Gamma(\underline{x}_{1},\underline{x}_{2}) = \sum_{\substack{i < j}} \Delta\Gamma_{ij}(\underline{x}_{m},\underline{x}_{n}) \qquad 2.1.44$$

The i and j values label the occupied spin-orbitals within the HF description and, hence, taken as a pair, (i,j) references the individual intra- and inter-electronic shells. The influence of electron correlation is examined here by evaluating the Coulomb hole  $\Delta f(r_{12})$ , the partial Coulomb holes  $\Delta g(r_{12}, r_1)$  and various one- and two-particle expectation values. Following Coulson and Neilson<sup>(63)</sup>, the

change in the distribution function  $f(r_{12})$  for the interparticle separation distance  $r_{12}$  is defined as

$$\Delta f(r_{12}) = \int \Delta \Gamma(\underline{x}_1, \underline{x}_2) \, d\underline{x}_1 d\underline{x}_2 / dr_{12} , \qquad 2.1.45$$

where the integration is over spin and all space coordinates except  $r_{12}$ . See Appendix A.2 for a general discussion of the formulation of the Coulomb hole. Thus, using equation (2.1.44), we may re-write (2.1.45) to give

$$\sum_{\substack{N=3\\\Delta f(r_{12}) \approx E \ \Delta f_{ij}(r_{12}) = E \ i \leq 1}}^{N=3} \Delta \Gamma_{ij}(\underline{x}_{1}, \underline{x}_{2}) d\underline{x}_{1} d\underline{x}_{2}/dr_{12} 2.1.46$$

and hence the Coulomb hole may be examined for each shell. Since each  $f_{ij}(r_{12})$  has been normalized to unity at both the correlated and HF level, it follows that

$$\int_{0}^{\infty} \Delta f_{ij}(r_{12}) dr_{12} = 0 . \qquad 2.1.47$$

Although the Weiss CI wavefunctions for the threeelectron ions account for large fractions of the correlation energy, their use in equation (2.1.43) implies that any restriction or limitation imposed by Weiss when determining his wavefunction will, of course, be reflected in our findings. This point will be of special relevance when reporting our analysis of correlation effects for the <sup>2</sup>P-state. We show in Table 2.1.2 the configurations which were considered in the two-particle density for each shell; the notation  $(xx)^{1}$ Sq and  $(xx)^{3}$ Sq, refers to the manner in which the spins of the two electrons are coupled to give a

singlet or triplet S symmetry, respectively. The resulting pair is then coupled with the third electron q to produce a doublet S state  $(^{2}S)$ .

In Figures 2.1.1(A-D) we illustrate the distribution function  $f(r_{12})$  at the HF level for each individual shell and the renormalized total density (which is given by  $(K\alpha K\beta)$ +  $K\alpha L\alpha + K\beta L\alpha)/3$ ). The Coulomb hole associated with the HF spin-orbital pair (i,j) is given in equation (2.1.46), and the result for the individual shells and the sum total for the Li-like ions are shown in Figures 2.1.2(A-D). It is to be noted that each  $r_{12}$ -axis has a Z scaling factor, where Z is the nuclear charge. Although calculations were performed for  $3 \leq 2 \leq 8$ , some results are presented only for the selected ions Li, Be<sup>+</sup> and N<sup>4+</sup>: the K $\alpha$ K $\beta$ -, K $\alpha$ L $\alpha$ - and KBLa-curves are compared with the sum total Coulomb hole, and the curves are shown in Figure 2.1.3. In Figure 2.1.4, we present, for the series of ions, the percentage (Y%) of the interparticle distribution function  $f_{HF}(r_{12})$ redistributed by correlation in each individual shell and the total.

Since the Coulomb holes are obtained from averaged distributions, it is of interest to evaluate the partial Coulomb holes  $\Delta g(r_{12}, r_1)$ . Following the procedure of Boyd and Coulson<sup>(64)</sup>, these "holes" are defined such that

$$\int \Delta g_{ij}(r_{12}, r_1) dr_1 = \int (g_{ij}(r_{12}, r_1)_{corr} - g_{ij}(r_{12}, r_1)_{HF}) dr_1$$
  
=  $\Delta f(r_{12})$  2.1.48

and, therefore, they enable us to examine the effect of

electron correlation when a test electron, say electron 1, is located at a specific distance from the nucleus. The functions  $g_{HF}(r_{12},r_1)$  and  $\Delta g(r_{12},r_1)$  for Li, Be<sup>+</sup> and N<sup>4+</sup> (for KaKβ-, KaLa- and KβLa-shells) are displayed as surfaces in Figures 2.1.5 and 6, respectively. N<sup>4+</sup> is chosen, rather than 0<sup>+5</sup>, so that some subsequent comparison will be possible with our current analysis of the <sup>2</sup>P-state reported by Weiss; his 0<sup>+5</sup>(<sup>2</sup>P) wavefunction is thought to be suspect.

## Two-particle expectation values

In addition to calculating the Coulomb hole, we have obtained insight into the shape of each  $f(r_{12})$  by evaluating the expectation values

$$\langle r_{12}^{n} \rangle = \int f(r_{12}) r_{12}^{n} dr_{12}$$
 2.1.49

for  $-1 \le n \le 2$ . Clearly, different regions of the  $f(r_{12})$ curve will be emphasised by each value of n. The spread or diffuseness of the two-particle distribution  $f(r_{12})$  about it's mean value  $\langle r_{12} \rangle$  is given by the standard deviation  $\Delta r_{12}$ , which is defined as

$$\Delta r_{12} = \int \left( \langle r_{12}^2 \rangle - \langle r_{12} \rangle^2 \right) . \qquad 2.1.50$$

In order to measure the angular correlation effects in different regions of the two-particle density, we calculated the expectation values

$$\langle \underline{r}_1 \cdot \underline{r}_2 / \underline{r}_1^n \underline{r}_2^n \rangle = \int \underline{r}_1 \cdot \underline{r}_2 / \underline{r}_1^n \underline{r}_2^n \Gamma_{ij}(\underline{r}_1, \underline{r}_2) d\underline{r}_1 d\underline{r}_2 = 2.1.51$$

where n = 0,1 and 2. Each of these expectation values assesses angular correlation, and we note that when n = 1 we obtain the purely angular expectation value  $\langle \cos \gamma \rangle$ , where  $\gamma$ is the angle between the electronic position vectors  $\underline{r}_1$  and  $\underline{r}_2$ . To calculate the expectation values defined by equation (2.1.51), it is necessary to evaluate an angular integral which contains a product of three spherical harmonics, i.e.

$$Y_{1m}^{*}(\theta\phi) Y_{1'm}^{*}(\theta\phi) Y_{1u}^{*}(\theta\phi).$$

The details concerning the calculation of this type of spherical harmonic integration, which is involved in equation (2.1.51), are discussed in the work of Reed<sup>(77)</sup>. The results for these expectation properties are shown in Table 2.1.3.

The radial correlation contained within a wavefunction may be investigated by evaluating the two-particle radial density distribution,  $D_{ij}(r_1,r_2)$ , in each individual electronic shell. This density is defined by

$$D_{ij}(r_1, r_2) = \int \Gamma_{ij}(r_1, r_2) r_1^2 r_2^2 d\Omega_1 d\Omega_2 , \qquad 2.1.52$$

where  $d\Omega_1$  denotes integration over all angular coordinates of the position vector  $\underline{r}_1$ , such that

 $\int D_{ij}(r_1, r_2) dr_1 dr_2 = 1 . \qquad 2.1.53$ 

Of particular interest is the change caused in  $D(r_1, r_2)$  by the introduction of correlation effects, therefore we have calculated

$$\Delta D_{ij}(r_1, r_2) = D_{ij}(r_1, r_2)_{corr} - D_{ij}(r_1, r_2)_{HF} , 2.1.54$$

and the results for  $D_{HF}(r_1, r_2)$  and  $\Delta D(r_1, r_2)$  are presented as surfaces in Figures 2.1.7-8. In addition, we have analyzed the change which occurs in the two-particle radial expectation values

$$\langle r_1^n r_2^n \rangle_{ij} = \int D_{ij}(r_1, r_2) r_1^n r_2^n dr_1 dr_2$$
 2.1.55

where  $-2 \leq n \leq 3$ .

## One-particle expectation values

In order to study the effect of electron correlation on the one-electron distribution in different regions of each individual electronic shell for a given atom, we have calculated the radial density function  $D_{ij}(r_1)$ , which is defined as

$$D_{ij}(r_1) = \int D_{ij}(r_1, r_2) dr_2$$
, 2.1.56

and the expectation values  $\langle r_1^n \rangle_{ij}$ , defined by

$$\langle r_1^n \rangle_{ij} = \int D_{ij}(r_1) r_1^n dr_1$$
, 2.1.57

when  $-2 \le n \le 3$ . If n = 0, equation (2.1.57) gives unity

for each (i,j)-pair where i<j. From equation (2.1.57), we see that the expectation values weight different regions of space and consequently they are useful for comparing density distributions arising from different wavefunctions. For example, the function  $r_1^{-2}$  becomes particularly large in regions close to the nucleus, thus comparison of  $\langle r_1^{-2} \rangle$  evaluated from two different wavefunctions indicates how similar their density distributions are near to the nucleus. By contrast, comparison of values of  $\langle r_1^3 \rangle$  indicates the similarity of density distributions in the outer regions of the charge clouds. As well as revealing correlation effects, some of the  $\langle r_1^n \rangle$  values are of considerable practical importance: for example, we can obtain the electron-nucleus attraction energy from  $\langle r_1^{-1} \rangle$ .

# Radial and Angular Correlation Coefficients

In 1968 Kutzelnigg and his colleagues<sup>(68)</sup> suggested that global effects of electron correlation in atoms and molecules may be analyzed in terms of so-called correlation coefficients  $\tau$ . These coefficients are based on the concepts of probability theory and mathematical statistics. To obtain a measure of the effects of radial correlation at large and small values of  $r_1$ , we have calculated the radial coefficients

$$\tau_{radial} = \frac{\langle r_1^n r_2^n \rangle - \langle r_1^n \rangle^2}{\langle r_1^{2n} \rangle - \langle r_1^n \rangle^2}$$
 2.1.58

where n = 1 and -1 corresponds to  $\tau_r$  and  $\tau_{1/r}$ , respectively.

To assess angular correlation we use the following coefficients

$$\tau_{\text{angular}} = \langle \mathbf{r}_1^{n-1} \ \underline{\mathbf{r}}_1 \cdot \underline{\mathbf{r}}_2 \ \mathbf{r}_2^{n-1} \rangle / \langle \mathbf{r}_1^{2n} \rangle \qquad 2.1.59$$

where n = 1, -1, 0 yields  $\tau_{\gamma}, \tau_{\gamma}$ . and  $\tau_{\gamma''}$ , respectively. These angular coefficients are related, in turn, to  $\langle \underline{r}_1, \underline{r}_2 \rangle$ ,  $\langle (\underline{r}_1/r_1^2), (\underline{r}_2/r_2^2) \rangle$  and  $\langle \cos \gamma \rangle$ , where  $\gamma$  is the angle between the electronic position vectors  $\underline{r}_1$  and  $\underline{r}_2$  for electrons 1 and 2. The selection of a particular  $\tau$  enables us to emphasize a specific region of the two-particle density when measuring angular effects. The radial correlation coefficients and the angular coefficients given above are dimensionless and, in each instance, they are bounded in absolute value by unity i.e.  $-1 \leq \tau \leq 1$ . For the angular coefficients in equation (2.1.60), a value of -1 indicates perfect negative correlation and implies that the position vectors are oppositely aligned, whereas a value of +1 represents perfect positive correlation signifying that the vectors are parallel. For consistency, we followed the definition of the Coulomb hole and hence the changes in each  $\tau$  due to electron correlation effects are given as

$$\Delta \tau = \tau_{\rm corr} - \tau_{\rm HF} \qquad 2.1.60$$

The results for  $\Delta \tau$  for each shell, and also for the total system, are presented in Table 2.1.8. The totals for  $\Delta \tau$  are obtained by using the sum totals for the appropriate expectation values to determine each total  $\tau$  at both the HF and correlated levels of description.

### CHAPTER 2.1.4

#### DISCUSSION

Although our main interests are in the effects of electron correlation, a brief discussion of the corresponding HF properties will be of interest. A comparison of the energies derived from the restricted Hartree-Fock (RHF) and the full CI wavefunctions of Weiss<sup>(25)</sup> is given in Table 2.1.1.

For convenience we will first discuss the intra-shell for the Li-like ions and then follow with a discussion of the inter-shell electron pairs and finally this discussion will be ended by the comparison of the total atom properties for the three-particle systems with those of the intra- and inter-shells.

## The KaKB-shell

Inspection of Figure 2.1.1(A) shows that, as Z increases, the maximum probability of the interparticle distribution function  $f_{HF}(r_{12})$  increases and it is also observed that the location of these maxima decreases as Z becomes larger. The Coulomb holes of the K-shell,  $\Delta f(r_{12})$ , are presented in Figure 2.1.2(A) for the Li-like ions. These holes are seen to possess coniderable similarity when plotted against the scaled co-ordinate  $Zr_{12}$ , where Z is the nuclear charge. However, one of the most striking features of these curves is that for Li and all members of the iso-electronic series the Coulomb holes possess the conventional

shape previously evaluated for the ground state of the helium-like electronic sequence; see, for example, Curl and Coulson<sup>(61)</sup> and Seddon and Banyard<sup>(69)</sup>. A corresponding similarity exists when comparing Figure 2.1.2(A) with the KαKβ- results for the Be-like ions; see Banyard and Mashat<sup>(28)</sup>. The balance between the positive and negative contributions for a given  $\Delta f(r_{12})$  curve is a consequence of the normalisation conditions on  $f_{corr}(r_{12})$  and  $f_{HF}(r_{12})$ whereas the magnitude and, in particular, the location of each extremum of a Coulomb hole gives valuable insight into the various effects introduced by correlation. Since the negative region of  $\Delta f(r_{12})$  indicates a reduction in  $f(r_{12})$ relative to the Hartree-Fock curve, the value of r<sub>12</sub> such that  $\Delta f(r_{12}) = 0$  may be interpreted as the radius of the Coulomb hole. It was found that this radius decreases as 2 increases whereas, by contrast, the minimum and maximum values for  $\Delta f(r_{12})$  show only small variations with Z. The Coulomb holes have radii of 0.66, 0.48, 0.26 and 0.23 for Li,  $Be^+$ ,  $B^{2+}$ ,  $N^{4+}$  and  $O^{5+}$ , respectively. Such results are comparable with previous work<sup>(28)</sup> i.e., the radii of the holes for the K-shell of the four-electron series which range from 0.23 to 0.66 a.u. and are ordered as  $0^{4+} < B^+ < C^+$ Be  $< Li^{-}$ . From Figure 2.1.2(A) we see that the zeros of the scaled  $\Delta f(r_{12})$  curves are in close agreement. An attempt was made to bring the present K-shell results into even better agreement for all  $r_{12}$  by using a scaling factor (Z - $\delta$ ). Greatest coincidence among the curves was achieved when the scaling parameter  $\delta$  was 0.38 ± 0.01 whereas, from previous work, the  $\delta$ -values were 0.41 ± 0.02 for the K-shell of Be-like<sup>(28)</sup> and 0.38 for the He-like ions<sup>(60)</sup>. The

similarity of such results is quite striking.

The Coulomb hole is clearly associated with the concept of a hole in the atomic or molecular charge cloud around any selected electron and can therefore be described in terms of its depth and radius  $({}^{63,70})$ . Consequently, a comparison within the series of ions can be obtained in terms of the percentage of each  $f_{\rm HF}(r_{12})$  probability density which was redistributed due to correlation; this quantity, labeled Y, is shown in Table 2.1.3 and Figure 2.1.4.

The behaviour of the Coulomb hole in the KaK $\beta$ -shell is reflected in the two-particle properties; in particular, the value of  $\langle r_{12}^{-1} \rangle$  bears a very close relationship to the percentage change of the density, Y%. In general, the results shown in Table 2.1.3 reveal that the smaller the value of  $\langle r_{12}^{-1} \rangle$ , the greater the value of Y%. This correspondence is due to the dependence of the Coulomb hole and  $\langle r_{12}^{-1} \rangle$  upon precisely the same region of the f( $r_{12}$ ) curve. In addition to this, the results shown in Table 2.1.3 reveal that the difference,

$$\Delta \langle r_{12}^{-1} \rangle = \langle r_{12}^{-1} \rangle_{corr} - \langle r_{12}^{-1} \rangle_{HF}$$

is a constant, independent of nuclear charge. For the He-like series, Curl and Coulson<sup>(61)</sup> found that numerically,  $\Delta \langle r_{12}^{-1} \rangle = -0.08$  a.u., whereas for the KaKβ-shell of the Li-like ions we obtained  $-0.085 \pm 0.001$ . From the Tables 2.1.4 & 9, the percentage of charge shifted, Y, and the percentage change in  $\langle r_{12}^{-1} \rangle$  vary almost linearly with  $z^{-1}$ .

Correlation produces an increase in the K-shell interparticle quantities  $\langle r_{12} \rangle$  and  $\langle r_{12}^2 \rangle$  for 3  $\langle$  2  $\langle$  8 whereas, by contrast,  $\Delta r_{12}$  is always decreased in value. This result is in agreement with the results for Be<sup>(65)</sup> and the Be-like ions<sup>(28)</sup>, and also with those for He<sup>(63)</sup> and the He-like ions<sup>(60)</sup>. The decrease in  $\Delta r_{12}$  indicates that the spread of the two-particle density about the mean interelectronic separation  $\langle r_{12} \rangle$  is reduced. From Table 2.1.4 it is observed that the  $\langle r_{12} \rangle$  and  $\langle r_{12}^2 \rangle$  expectation values are greater in a three-electron system than those for identical Z in the two- and four-electron series. This comparison holds for both the HF and correlated descriptions of the K $\alpha$ K $\beta$ -shells.

The quantities  $\langle (\underline{r}_1/r_1^n), (\underline{r}_2/r_2^n) \rangle$ , where n = 0, 1 and 2, each assess angular correlation but with stress being placed different regions of the two-particle density. As shown on in Table 2.1.3, when n = 0 and 1, the value of these components at the correlated level decreases as Z increases whereas, when n = 2, the expectation value increases with 2. At the HF level these quantities are, of course, identically zero, so they are not included in Table 2.1.3. At the correlated level, these quantities are seen to be of negative sign. Therefore, angular correlation enhances the probability that  $\gamma$  (the angle between the electron position vectors  $\underline{r}_1$  and  $\underline{r}_2$ ) will be greater than 90° and decreases the probability that  $\gamma$  is less than 90°. Returning to Table 2.1.4, the comparison in the  $K\alpha K\beta$ -shell for the above quantities can be made between Be, Be<sup>+</sup> and Be<sup>2+</sup>. It is

clear that  $Be^+ \rightarrow Be \rightarrow Be^{2+}$ , and therefore we may conclude that the addition of one 2s-electron or two 2s-electrons to  $Be^{2+}$  causes the value of the angular correlation expectation properties in the KaK $\beta$ -shell to be increased slightly in magnitude. There was no steady increase in going from one to two 2s-electrons. For the KaK $\beta$ -shell we see that  $\langle \underline{r}_1, \underline{r}_2 \rangle$ in the Li-like ions is greater than the corresponding quantity for the Be-like ions, but as Z increases both magnitudes become smaller and get closer. For example,  $\langle \underline{r}_1, \underline{r}_2 \rangle = -.0177$ , -.0069, -.0033 and -.0008 for Li<sup>-</sup>, Be, B<sup>+</sup> and  $0^{4+}$ , respectively whereas  $\langle \underline{r}_1, \underline{r}_2 \rangle = -.0179$ , -.00707, -.00348 and -.0008 for Li, Be<sup>+</sup>, Be<sup>2+</sup> and  $0^{5+}$ , respectively.

The  $g_{HF}(r_{12},r_1)$  and  $\Delta g(r_{12},r_1)$  surfaces for the KaK $\beta$ shell are presented in Figures 2.1.5(A) and 2.1.6(A). The partial Coulomb holes in Figure 2.1.6(A) show the change in behaviour of the Coulomb hole as the position of the test electron is varied. The K-shell diagrams for Li, Be<sup>+</sup> and  $N^{4+}$  show that the largest hole occurs when  $r_1 \approx r_K$ . We see in the  $\Delta g$  surfaces a decrease in density on the near-side of the nucleus  $(r_{12} < r_1)$  and an increase on the far-side  $(r_{12}$ >  $r_1$ ). It is seen that the greatest reduction in  $\Delta g(r_{12}, r_1)$ occurs at the diagonal  $r_{12} = r_1 \approx r_K$  for the KaKβ-shell in Li-like ions. All the features mentioned above for the  $\Delta g$ surfaces appear to be similar in shape to the <sup>1</sup>S intra-shell surface in  $Be^{(65)}$ , and in  $Li^{+(71)}$ . From Figures 2.1.5(A) -6(A), with support from Table 2.1.5, the  $g_{HF}(r_{12},r_1)$  and  $\Delta g(r_{12}, r_1)$  surfaces show obvious differences for changing Z. As Z increases these surfaces become less diffuse and increase in magnitude. Finally, there appears to be no

connection between the location of the maximum on a given  $g_{HF}(r_{12},r_1)$  surface and the locations of the maxima and minima on the corresponding  $\Delta g(r_{12},r_1)$  surface.

Consider now the influence of correlation on the two-particle radial distribution  $D_{HF}(r_1, r_2)$ , as shown by  $\Delta D(r_1, r_2)$ . As expected, the maximum of  $D_{HF}(r_1, r_2)$  is along the diagonal. It can be seen that  $\Delta D(r_1, r_2)$  has a negative region along the  $r_1 = r_2$  axis but it has a positive region when  $r_1$  is small and  $r_2$  is large and viceversa. The deepest negative region occurs when  $r_1 = r_2 = small$ , whilst a less negative region exists when  $r_1 = r_2 = large$ . As shown in Figures 2.1.7(A) - 8(A) the K-shell diagrams of  $D_{HF}(r_1, r_2)$ and  $\Delta D(r_1, r_2)$  become less diffuse and increase in magnitude From Table 2.1.6 - 7 the correlationas 2 increases. induced changes in  $\langle r_1^{-1}r_2^{-1} \rangle$  and  $\langle r_1r_2 \rangle$  give a measure of the influence of the radial correlation alone on the twoparticle density with the emphasis being placed roughly on those regions located at a distance of  $\langle r_1^{-1} \rangle$  and  $\langle r_1 \rangle$ respectively, from the nucleus. Inspection of  $\langle r_1^n \rangle$ , shown in Table 2.1.7, reveals a tendency for the correlated density to become marginally more diffuse than that obtained from the independent particle model (HF). Such a movement of density is not unexpected. The presence of the radial correlation within the wavefunction tends to keep the electrons apart. Consequently, the probability density might be expected to experience some radial expansion, relative to the HF model. A comparison of the correlated and HF values for  $\langle r_1 \rangle$  and  $\Delta r_1$  for the KaK<sub>β</sub>-shell shows that, not surprisingly, the effect becomes negligible as Z

increases. However, for a given Z, inclusion of electron correlation within the K-shell decreases the values of  $\langle r_1^n \rangle$  and  $\langle r_1^n r_2^n \rangle$  when n > 0 and increases these values when n < 0 when compared with the HF values. It is also found that the relation  $\langle r_1^{-2} \rangle \rangle \langle r_1^{-1} \rangle \rangle \langle r_1 \rangle \rangle \langle r_1^2 \rangle \rangle \langle r_1^3 \rangle$  will fit all the ions.

To aid further comparison, we may compare the one- and two-particle properties for the K-shell with the corresponding values for both the Be-like series<sup>(28)</sup> and the He-like series<sup>(60)</sup>. In the comparison of the one-particle expectation values  $\langle r_1^n \rangle$ , it is found that Be  $\rangle$  Be<sup>2+</sup>  $\langle$  Be<sup>+</sup> when n  $\rangle$  0 and Be  $\langle$  Be<sup>2+</sup>  $\rangle$  Be<sup>+</sup> when n  $\langle$  0. The same relationships were found when comparing 0<sup>4+</sup>, 0<sup>5+</sup> and 0<sup>6+</sup>. It seems that adding one L-shell electron or two L-shell electrons to Be<sup>2+</sup> causes the K-shell density to become slightly more diffuse. The cause of this expansion may perhaps be due to the L-shell electron providing some partial screening of the nucleus, hence permitting the K-shell electrons to drift outward slightly.

The changes in  $\tau$  provide a global measure of electron correlation because each coefficient involves expectation values based on both the one- and two-particle densities. The results are shown in Table 2.1.8. Figure 2.1.10 shows that for  $\Delta \tau_{\gamma}$ ,  $\Delta \tau_{\gamma'}$ ,  $\Delta \tau_{\gamma'}$  and  $\Delta \tau_{1/r}$  the variation with 1/2 is almost linear whereas, for  $\Delta \tau_{r}$ , a slight curvature can be observed. The results for  $\Delta \tau_{r}$ ,  $\Delta \tau_{1/r}$  and  $\Delta \tau_{\gamma}$  are essentially unchanged, to within graphical accuracy, when compared with the corresponding results for the Be-like

ions<sup>(28)</sup>. Finally, the comparison of the K-shells within the three-particle systems, can also be made by considering the percentage change in one- and two-particle properties within the system due to correlation. The results are shown in Table 2.1.9.

## The KaLa- and KBLa- shells

The interparticle distribution  $f_{HF}(r_{12})$  for the KaLa and KBLa intershells of the Li-like ions is shown in Figure 2.1.1(B-C). The general Z dependence is seen to follow that observed for the K-shell. The distribution functions f<sub>HF</sub>(r<sub>12</sub>) for the inter-shells display several interesting At small  $r_{12}$ , the  $f(r_{12})$  distribution function features. will be influenced mainly by the electron pair behaviour when the outer electron has penetrated the K-shell. For the KaLa curve, the existence of the Fermi effect produces a flat region at small  $r_{12}$  whereas, by marked contrast, the KBLa curve is seen to possess a small local maximum. Clearly, when the K- and L-shell electrons have different spin assignments but are both described by orbitals of s-type symmetry, a double occupancy can occur in the K-shell region with characteristics similar to those for KaKß. Probability arguments supports the observation that this local maximum in the KBLa curve is of much reduced magnitude by comparison with the K-shell results. For convenience in subsequent discussion, such behaviour will be refered to as a 'mini K-shell' effect.

The effect of electron correlation for the like- and unlike-spin assignments in the inter-shells can be seen by examining the Coulomb holes presented in Figures 2.1.2(B -C). The  $\Delta f(r_{12})$  curves not only reveal correlation effects but, naturally, reflect the main features of the  $f_{HF}(r_{12})$ curves. For a given ion the behaviour of the KaLa and KBLa Coulomb holes at large  $r_{12}$  is very similar. Since the spin of the third electron is different in the two cases, we suspect that this electron will have only an average rather than a specific effect on our results. The diagrams for KaLa and KBLa show that, as Z increases, this effect is very similar to the 2<sup>3</sup>S behaviour found by Boyd and Katriel<sup>(62)</sup> a series of two- electron systems. The relative for magnitude of the KaLa and KBLa Coulomb holes is indicated by the Y values in Table 2.1.3 and Figure 2.1.4. These percentage shifts in probability density are, naturally, much smaller than the  $K\alpha K\beta$ -shell value. From the comparison between the KaLa- and KBLa-shells, it is observed that the spread between the maximum and minimum values of  $\Delta f(r_{12})$  is greater in the  $K\beta L\alpha$ -shells that in the  $K\alpha L\alpha$ -shells.

The  $g_{HF}(r_{12},r_1)$  and  $\Delta g(r_{12},r_1)$  diagrams for KaLa- and K $\beta$ La-shells show the change in behaviour of the interparticle probability functions as the position of the test electron is varied. These surfaces are presented in Figures 2.1.5(B - C) and 2.1.6(B - C) for Z = 3, 4 and 7. Following the K-shell discussion, we begin with comments on the  $g_{HF}(r_{12},r_1)$  surfaces. These surfaces have their main characteristics located about the  $r_{12} = r_1$  diagonal line and parallel to the  $r_{12}$  axis for small  $r_1$ . In addition, and as

expected, when Z increases the pattern contracts towards the origin and the magnitude of these densities increases. The diagonal distribution is again asymmetric with the  $r_{12} = r_1$  axis: the maximum is always slightly on the right hand side (RHS) of the  $r_{12} = r_1$  axis for any selected and fixed  $r_1$  value outside the K-shell.

From the comparison between the  $g_{HF}(r_{12},r_1)$  surfaces for the KaLa- and KBLa-shell, it can be seen that a difference exists only at  $r_{12} = r_1 \approx r_K$ . Since there is no Fermi effect in K $\beta$ L $\alpha$ , the behaviour of the g(r<sub>12</sub>,r<sub>1</sub>) function has characteristics similar to those for the K-shell surface but is of much reduced magnitude, this feature is of course appropriate to the occurrence of a mini K-shell effect as discussed above. It can also be seen that the removal of this mini K-shell density causes the main characteristics to move towards the origin slightly. Consider now the  $\Delta g(r_{12}, r_1)$  surfaces for the KaLa- and K $\beta$ La-shells. When  $r_1$ is small, the test electron is located in the K-shell and the  $\Delta g$  vs.  $r_{12}$  behaviour illustrates the effects of correlation on the L-shell electron. On the other hand, when the test electron is located in the L-shell, the  $\Delta g$  vs. r<sub>12</sub> characteristics are largely a result of correlation effects within the K-shell. Returning to the KaLa partial Coulomb hole, which is shown in Figure 2.1.6(B), the diagram shows that when  $r_1$  is small, i.e. the test electron is in the K-shell, the flat region could be expected for small  $r_{12}$ due to the Fermi effect. The Fermi effect has caused a slight expansion in the KaLa characteristics compared with the KBLa surface, where no Fermi effect exists. In

contrast, the K $\beta$ L $\alpha \Delta g(r_{12}, r_1)$  surface shows a mini K-shell effect at  $r_1 \approx 0.3$  and  $r_{12} \approx 1$  for the example of Li. In addition , the comparison between K $\alpha$ L $\alpha$  and K $\beta$ L $\alpha \Delta g(r_{12}, r_1)$ shows the same inter-relationship as was found by Banyard and Youngman<sup>(66)</sup> in their examination of the 2<sup>1</sup>S and 2<sup>3</sup>S-states for He.

However, in the present case, it is to be noted that, for Li, there is an additional small positive hump at  $r_{12} \approx$ 5 and  $r_1 \approx 0.3$  in both inter-shell surfaces. These humps may be due to the averaged effect of the third electron which, for the inter-shell electron pairs, resides in the K-shell. Angular correlation effects in the inter-shells indicate an opening-up of the angle between the electronic position vectors  $\underline{r}_1$  and  $\underline{r}_2$  to values greater than 90°, see for example  $\langle \cos\theta_{12} \rangle$  in Table 2.1.3. Thus, a reduced screening of the nucleus by the K-shell electron can occur and, therefore, the L-shell density can drift inwards towards the origin, as was found in the He study (66). These surfaces are, as expected, slightly contracted towards the origin (nucleus) when compared with the He  $2^{1}$ S and  $2^{3}$ S states, due of course to the higher 2 value in Li. As 2 increases throughout the Li-like series, an examination of the  $\Delta g(r_{12}, r_1)$  surfaces for KaLa shows that the ordering of the absolute minimum and absolute maximum changes, i.e., the partial Coulomb hole for Z = 3 has a range of -0.002 to +0.003, whereas when Z = 7 the  $\Delta g$  has a range of -0.014 to +0.013. The  $\Delta g(r_{12}, r_1)$  values become larger as Z increases, and the absolute minimum of  $\Delta g$  increases by about 0.003 as 2 increases by unity throughout the series.

We now examine the  $D(r_1, r_2)$  densities at the HF level for the inter-shells. These radial probabilities of finding simultaneously the first electron at a distance  $r_1$  and the second one at a distance  $r_2$  from the nucleus are shown in Figure 2.1.7 as surface diagrams for the KaLa and K $\beta$ La shells. The  $D_{HF}(r_1, r_2)$  surface for K $\beta$ L $\alpha$  shows three arrangements having a high probability. These consist of two regions in which one electron is near the nucleus and the other further away, and a third region in which both electrons are near the nucleus. The  $D_{HF}(r_1, r_2)$  surface for KaLa shows only two arrangements of high probability, one electron being close to the nucleus and the other further away. For KaLa, the  $D_{HF}(r_1, r_2)$  gives zero probability for  $r_1 = r_2$ ; i.e. electrons with parallel spin tend to stay apart, so there is no possibility of the electrons being in the same region.

Examination of the one particle radial densities  $D_{HF}(r_1)$ in the inter-shells for Z = 3 shows that the location of the most probable value of the K- and L-shell can be found at  $r_1$ = 0.36 and 3.10 respectively. Figure 2.1.9 shows the one particle radial density  $D_{HF}(r_1)$  for the KaK $\beta$ -, KaLa- and K $\beta$ La- shells for the selected ions Li, Be<sup>+</sup> and N<sup>4+</sup>.

Let us now consider  $\Delta D(r_1, r_2)$  for the inter-shells when Z = 3. From Figure 2.1.8, correlation reduces the twoparticle density at  $r_1$  > radius of the L-shell and increases the density at K-radius <  $r_1$  < L-radius. This means that probability density will be taken from outside the L-shell

and placed between the K- and L-shells, when correlation is introduced. Except at small  $r_1$  and  $r_2$  we see that the general characteristics of the two inter-shell surfaces are quite similar. However, for the K $\beta$ L $\alpha$ -shell at small  $r_1 = r_2$ , we observe that  $\Delta D(r_1, r_2)$  has a behaviour very much like that for the doubly-occupied K-shell, i.e. the density is decreased along the  $r_1 = r_2$  diagonal axis and increased in the off-diagonal regions. Therefore, in this local region the density shifts are in accord with the usual "in-out" radial correlation effect. For the K $\alpha$ L $\alpha$ -shell, the Fermi effect stops the occurrence of such a feature.

Comments are now made regarding the one-particle expectation values for the inter-shells. The comparison between  $\langle r_1^n \rangle$  for Be<sup>+</sup> and Be<sup>(28)</sup> shows that the one-particle radial density for Be<sup>+</sup> in the KaLa-shell is more contracted towards the origin than those in Be, i.e. the  $\langle r_1^n \rangle$  results for Be<sup>+</sup>  $\rangle$  Be when n = -1, -2 and Be<sup>+</sup>  $\langle$  Be when n = 1, 2. The influence of correlation on the one-particle expectation values  $\langle r_1^n \rangle$  for KaLa has caused D(r<sub>1</sub>) to become more contracted towards the origin. As above, the changes in  $\langle r_1^n r_2^n \rangle$  are caused by a contraction of D(r<sub>1</sub>,r<sub>2</sub>) toward the nucleus.

Finally the total  $f_{HF}(r_{12})$  and  $\Delta f(r_{12})$  are presented in Figures 2.1.1(D) and 2.1.2(D). The relative magnitudes of the KaK $\beta$ -, KaLa-, K $\beta$ La- and the 'total' holes are shown in Figure 2.1.3 for Li, Be<sup>+</sup> and N<sup>4+</sup>. From Figure 2.1.3 the 'total' hole seems dominated by the K-shell whereas the KaLa- and K $\beta$ La contributions cause small change. A relative

measure of the  $K\alpha K\beta$ -,  $K\alpha L\alpha$ -,  $K\beta L\alpha$ - and normalized 'total' holes are provided by the corresponding Y values in Table 2.1.3.

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## CHAPTER 2.1.5

### SUMMARY

have examined the influence of electron correlation We the KaK $\beta$ -, KaLa- and K $\beta$ La-shells within the ground state on a series of Li-like ions. This has been achieved by of using a density partitioning technique in conjunction with the definition of the Coulomb hole introduced by Coulson and Neilson<sup>(63)</sup>. We have investigated the concept of the Coulomb hole  $\Delta f(r_{12})$  in position space. The balance between the positive and negative contribution for a given  $\Delta f(r_{12})$ curve is a consequence of the normalization conditions on f<sub>corr</sub> and f<sub>HF</sub>, whereas the magnitude and, in particular, the location of each extremum of a Coulomb hole gives valuable insight into the various effects introduced by correlation. The KaLß Coulomb hole appears to be much the same as those obtained for the doubly occupied K-shells of the corresponding He- and Be-like ions. The shape of the Coulomb holes is governed by the effects of radial and angular correlation which, in position space, are known to work in unison. This feature has been supported by examining the radial and angular correlation coefficients, When plotting  $\Delta f(r_{12})$  for the KaK<sub>β</sub>-shell in Li, Be<sup>+</sup>, τ.  $B^{2+}$ ,  $N^{4+}$  and  $O^{5+}$  against  $2r_{12}$ , the zeros of these holes became almost coincident. They could be brought into a higher degree of coincidence by using a scaling factor (Z +  $\delta$ ); the scaling parameter  $\delta$  was found to be only 0.38  $\pm$ 0.01, which is in close agreement with the  $\delta$  value of 0.38 for He-like ions (60) and 0.41 ± 0.02 for the K-shells of the

Be-like ions<sup>(28)</sup>. As found in the four-electron series, the radii of the holes for the K-shell of the three-electron systems are ordered as Li > Be<sup>+</sup> > B<sup>2+</sup> > N<sup>4+</sup> > 0<sup>5+</sup>. For the inter-shells, the Coulomb holes in the Li-like ions showed marked differences in behaviour at small r<sub>12</sub>. In addition, we found that the  $\Delta f(r_{12})$  values for KBLa were noticeably larger than those for the KaLa inter-shell, a result which is not surprising in view of the Fermi correlation present in the latter shell. From the relative magnitudes of the  $K\alpha K\beta$ -,  $K\alpha L\alpha$ -,  $K\beta L\alpha$ - and total holes we conclude that the Coulomb hole for a given whole atom is dominated by the K-shell contribution. The comparison between the individual shells and the total effects can be made by inspection of the percentage of each  $f_{HF}(r_{12})$  density which has been redistributed as a result of correlation. It was observed that in the K-shell, the depth of the Coulomb hole bears a very close relationship to the interparticle expectation value  $\langle r_{12}^{-1} \rangle$ , since the later value gives directly the electron-electron repulsion energy. Consequently, the expectation value  $\langle r_{12}^{-1} \rangle$  may be related to the percentage change Y%. For the intra-shell, we have investigated the quantities  $\langle r_1^n, r_2^n \rangle$  for Li<sup>+</sup>, Li and Li<sup>-</sup> and also for B<sup>2+</sup>, Be<sup>+</sup> and Be. We found that the correlated angular expectation properties in the KaKβ-shell increased as we added the one or two 2s electrons to  $\text{Li}^+$  or  $\text{Be}^{2+}$ .

Determination of the Coulomb holes as a function of  $r_1$  has revealed that the correlation characteristics are very dependent on the location of the test electron. For example, for the inter-shell diagrams for  $\Delta g(r_{12}, r_1)$ , the  $r_1$ 

value may be chosen to locate the test electron in either the K-shell or L-shell regions whereas, for the KaKB-shell, all r<sub>1</sub> values refer to the test electron being in the K-shell. The  $K_{\alpha}K_{\beta}$ -diagrams for Li, Be<sup>+</sup> and N<sup>4+</sup> each showed that when  $r_1 \approx r_K$ , a reduction in density occurred on the near-side of the nucleus with respect to the test electron  $(r_{12} < r_1)$  and an increase was observed on the far-side  $(r_{12} < r_1)$ Such results are clearly in keeping with our > r<sub>1</sub>). intuition and, indeed, are physical seen in the corresponding diagrams obtained by Banyard and Mobbs<sup>(65)</sup> for Be, and by Banyard and Reed for Li<sup>+(71)</sup>. For the intershells, a comparison of KaLa with KBLa for each system showed a similarity in the  $\Delta g(r_{12}, r_1)$  surfaces when  $r_1 \approx r_L$ whereas, when  $r_1 \approx r_{K}$  the surfaces show differences which are directly attributable to the influence of Fermi correlation in the KaLa-shells. This comparison between the  $\Delta g$ -sufaces for KaLa and K $\beta$ La seems to be similar to that found by Banyard and Youngman<sup>(66)</sup> in the study of the 2<sup>1</sup>S and 2<sup>3</sup>S states for He. The diagrams of the partial Coulomb holes and the  $\Delta D(r_1, r_2)$  for each shell become less diffuse and increase in magnitude as Z increases.

Finally, although we have examined only the Z-dependent trends within individual electronic shells, it should be realized that the partitioning technique used here does allow us to perform a comparative analysis of different CI wavefunctions for any given system<sup>(65)</sup>.

Tables and Figures - Part 2.1

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2	£	4	S	9	7	8
ЯН	7.43272	14.27740	23.37599	34.72606	48.32685	64.17805
Correlated	7.47710	14.32350	23.42312	34.77384	48.37509	64.22661
Experimental	7.47807	14.32479	23.42471	34.77573	48.37728	64.22917
\$E corr	97.9	97.3	96.7	96.2	95.7	95.0
۲ (۳)	0.998143	0.998902	0.999337	0.999255	0.999633	0.999784

Table 2.1.1 Wavefunction energies and correlation energies and overlap intergrals between correlated<sup>(25)</sup> and HF<sup>(26)</sup> wavefunctions. Note that all energies The percentage correlation energy is defined as  $s_{E_{corr}} = 100(E_{corr} - E_{HF})/(E_{exp} - E_{HF})$ are negative and are expressed in Atomic Units.

	Number an	d type of	correlatio	n configur	ations con	sidered pe	r shell
SHELL	(ss) <sup>1</sup> Ss	{pp} <sup>1</sup> Ss	{dd} <sup>1</sup> Ss	{ff} <sup>1</sup> Ss	{gg} <sup>1</sup> Ss	{pp} <sup>3</sup> ss	(dd) <sup>3</sup> Ss
Κα Κβ	18	12	7	3	-	ο	0
KaLa	18	ο	0	0	0	£	-
KBLa	18	12	7	£	-	£	-

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A summary of the correlation configurations and type considered in the two-particle density for each shell. **Table 2.1.2** 

	- F	$ r_{1}^{n} - r_{2} $	/r <sup>n</sup> >			< r <sup>n</sup> 1	2 >			Δ	r <sub>12</sub>	
Z SHEL	L = 2	n = 1	n = 0	R		n U	-	r	= 2			<b>8</b> 9 X
	CORR	CORR	CORR	HF	CORR	HF	CORR	HF	CORR	HF	CORR	
Κα Κβ	0.22349	0.04461	0.01792	1.6501	1.5654	0.8396	0.8637	0.8937	0.9303	0.4346	0.4293	3.045
3 KBLa	0.00644	0.00938 0.01013	0.02346	0.3227	0.3220	3.9215	3.9047	18.1710	19.9729	1.6712	1.6512	0.460
Tota	1 0.07982	2 0.02137	0.02119	0.7604	0.7322	2.8959	2.8923	12.4119	12.2907	1.2549	1.2405	1.266
KaKB	0.31564	1 0.03341	0.00707	2.2748	2.1893	0.6072	0.6202	0.4663	0.4807	0.3124	0.3101	2.212
Kala	0.01393	3 0.00925	0.00987	0.5127	0.5126	2.3313	2.3294	6.3340	6.3150	0.9481	0.9430	0.130
4 KBLa	0.02211	1 0.01098	0.01179	0.5484	0.5447	2.3249	2.3252	6.3341	6.3232	0.9639	0.9575	0.277
Tota	1 0.1172	3 0.01788	0.00958	1.1120	1.0822	1.7545	1.7583	4.3781	4.3730	0.7415	0.7369	0.808
K a K B	0.4084	9 0.02672	0.00348	2.9025	2.8166	0.4754	0.4835	0.2855	0.2927	0.2443	0.2430	1.734
Kala	0.0214	6 0.00813	0.00492	0.7079	0.7072	1.6799	1.6807	3.2730	3.2739	0.6714	0.6702	0.116
5 KBLa	0.0351	6 0.01005	0.00619	0.7658	0.7601	1.6737	1.6762	3.2731	3.2775	0.6868	0.6841	0.264
Tota	10.1550	4 0.01497	0.00486	1.4587	1.4280	1.2763	1.2801	2.2772	2.2814	0.5342	0.5324	0.617
KaKB	0.5947	9 0.01904	0.00121	4.1454	4.0622	0.3316	0.3355	0.1384	0.1410	0.1690	0.1685	1.204
KaLa	0.0364	5 0.00628	0.00172	1.0906	1.0888	1.0858	1.0870	1.3616	1.3641	0.4273	0.4272	0.113
7 KBLO	0.06174	4 0.00807	0.00228	1.1946	1.1843	1.0803	1.0828	1.3614	1.3656	G04400	0.4394	0.248
Tota	10.2309	9 0.01113	0.00174	2.1435	2.1118	0.8326	0.8351	0.9538	0.9569	0.3456	0.3450	0.423
KαKB	0.6868	1 0.01664	0.00080	4.7955	4.6889	0.2847	0.2909	0.1035	0.1060	0.1489	0.1463	1.042
KaLa	0.0440	4 0.00560	0.00112	1.2802	1.2782	0.9239	0.9250	0.9846	0.9870	0.3619	0.3624	0.112
8 KBLa	0.0751	4 0.00725	0.00151	1.4044	1.3954	0.9192	0.9211	0.9847	0.9880	0.3739	0.3735	0.225
Tota	11 0.2686	6 0.00983	0.00114	2.4934	2.4542	0.7093	0.7123	0.6909	0.6937	0.2949	0.2941	0.370
Table	2.1.3 S(	ome two-p	article e	expectat	cion prof	erties f	or the	$(1s^{2}z_{s})^{2}$	5 state 1	or the i	ndividua	l shells
	ai	nd the	normalize	ed Totá	al value:	for the	ti-lik	e ions.	Also lis	sted is t	che perce	ntage of
	<b>t</b> I	he inter	-particle	e distı	ribution	functic	n f <sub>Hf</sub> (r.	12) which	h has bee	en re-dis	stributed	. These
	ū	esults ai	e derive	d by us:	ing Weis:	s <sup>(25)</sup> cI	and Wei	ss (HF Wa	vefunctic	n.		

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	<cosy></cosy>	<r 1.="" 1.<="" th=""><th>ζΓ,</th><th>12&gt;</th><th><r></r> <r></r> <r></r> <r></r> </th></r>	ζΓ,	12>	<r></r> <r></r> <r></r> <r></r>	<u>^</u>	۵r	12
	CORR	CORR	HF	CORR	HF	CORR	HF	CORR
Li <sup>+</sup>	-0.0437	-0.0172	0.8383	0.8622	0.8906	0.9265	0.4334	0.4279
Li	-0.0446	-0.0179	0.8395	0.8637	0.8937	0.9303	0.4346	0.4293
Li <sup>-</sup>	ł	-0.0177	0.8393	0.8623	0.8927	0.9274	0.4339	0.4286
Be <sup>2+</sup>	-0.0329	-0.0069	0.6058	0.6187	0.4637	0.4777	0.3109	0.3081
₽°+	-0.0334	-0.0071	0.6072	0.6200	0.4661	0.4804	0.3121	0.3098
Be	-0.0331	-0.0070	0.6071	0.6194	0.4660	0.4795	0.3121	0.3096

The results for Li<sup>+</sup> and Be<sup>2+</sup> are taken from Banyard and Seddon<sup>(60)</sup>, and Seddon and Banyard<sup>(69)</sup>. For Li<sup>-</sup> and Be (except  $\langle \mathbf{I}_1^n, \mathbf{I}_2^n \rangle$ ) the results are taken from Banyard and Mashat<sup>(28)</sup>. The  $\langle {\tt I}_1, {\tt I}_2^n \rangle$  values for Be are taken from Table 2.1.4 Comparisons for the K-shell within the two- three- and four-electron system. Banyard and Mobbs<sup>(65)</sup>.

MININUM	MUMINIM	MUMINIM	MUMINIM	MUMI		r <sub>12</sub> value		MAX	MUMI		MAXIF		
						when $r_{,=0}$ and							-
н г	с) Q	r,)	r12	н,	Δg(r <sub>12</sub> ,r <sub>1</sub> )	Δg(r <sub>12</sub> ,r <sub>1</sub> )=0	r12	н Н	Δg(r <sub>12</sub> ,r <sub>1</sub> )	r 12	r1 9	$g_{\mathrm{HF}}(r_{12},r_{1})$	
0.36	-	.40	0.30	0.30	-0.171	0.50	0.85	0.30	+0.077	0.50	0.35	1.977	
0.26	*	.87	0.20	0.20	-0.235	0.35	0.60	0.25	+0.104	0.35	0.25	3.775	
0.15	e	.48	0.12	0.12	-0.416	0.20	0.34	0.14	+0.194	0.20	0.14	12.604	<u></u>
0.13	4	.01	0.10	0.10	-0.478	0.16	0.30	0.12	+0.222	0.16	0.12	16.668	

The location and value of the maxima and minima in the  $g(r_{12},r_1)$  and  $\Delta g(r_{12},r_1)$ surfaces for the K $\alpha$ K $\beta$ -shell for the (1s<sup>2</sup>2s)<sup>2</sup>S state for Li, Be<sup>+</sup>, N<sup>4+</sup> and 0<sup>5+</sup>. **Table 2.1.5** 

						< r <sup>n</sup> r <sup>1</sup>	^				
2	SHELL	r	= -2	- -		1 2		H L	2	" L	e
		HF	CORR	HF	CORR	HF	CORR	HF	CORR	HF	CORR
m	KaKA	222.669	193.884	7.2093	7.0033	0.3285	0.3211	0.1996	0.1845	0.1957	0.1697
	KaLa	1.902	1.941	0.8520	0.8600	2.2035	2.1866	7.8282	7.7061	40.9205	39.8887
	KBLa	6.480	5.854	0.9274	0.9283	2.2198	2.2045	7.9210	7.7980	41.4453	40.3250
	Total	76.684	67.229	2.9962	2.9306	1.5839	1.5707	5.3163	5.2294	27.5205	26.7939
4	KαKβ	770.782	702.440	13.5602	13.2911	0.1722	0.1698	0.0543	0.0518	0.0274	0.0253
	KαLα	10.033	10.158	1.9774	1.9892	0.9331	0.9291	1.3845	1.3730	2.9903	2.9507
	KβLα	40.240	36.532	2.2363	2.2249	0.9469	0.9439	1.4218	1.4099	3.0866	3.0349
	Total	273.685	249.708	5.9246	5.8351	0.6841	0.6809	0.9535	0.9449	2.0348	2.0037
ß	KαKβ	1991.944	1855.867	21.9078	21.5771	0.1058	0.1047	0.0204	0.0197	0.0062	0.0059
	KαLα	31.231	31.505	3.5058	3.5210	0.5222	0.5206	0.4307	0.4282	0.5143	0.5098
	KβLα	133.073	122.477	4.0403	4.0139	0.5323	0.5313	0.4466	0.4441	0.5377	0.5311
	Total	718.749	669.928	9.8180	9.7038	0.3867	0.3855	0.2992	0.2973	0.3528	0.3489
2	ΚαΚβ	8164.822	7785.325	<b>44</b> .5988	44.1498	0.0515	0.0512	0.0048	0.0047	0.0007	0.0007
	ΚαΙα	152.840	153.642	7.7920	7.3132	0.2332	0.2327	0.0853	0.0850	0.0450	0.0447
	ΚβΙα	683.526	641.886	9.1450	9.0844	0.2389	0.2387	0.0895	0.0892	0.0477	0.0473
	Τοtal	3000.396	2860.286	20.5119	20.3492	0.1745	0.1742	0.0895	0.0596	0.0311	0.0309
60	KaKβ	14213.760	13646.583	58.9433	58.4395	0.0389	0.0386	0.0027	0.0027	0.0003	0.0003
	KaLa	279.547	280.800	10.5521	10.5763	0.1718	0.1715	0.0463	0.0461	0.0179	0.0178
	KβLa	1264.958	1196.170	12.4469	12.3671	0.1763	0.1762	0.0487	0.0485	0.0191	0.0190
	Total	5252.755	5041.185	27.3141	27.1276	0.1763	0.1288	0.0326	0.0324	0.0124	0.0124
Tal	0 <b>1e 2</b> .1	.6 Expect the 1 using	tation val normalized Weiss <sup>(25)</sup>	tues <r<sup>n Total CI and W</r<sup>	r <mark>r</mark> > r2 values f( eiss(26)	the (1s <sup>2</sup> or the Li <b>HF wavef</b>	2s) <sup>2</sup> s st -like ic unctions	ate for ns. The	the indi se resu	ividual s lts are d	hells and lerived b

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		2	= -2	" "	-		-	= u	2	" "	. 3		
2	SHELL	HF	CORR	HF	CORR	HF	CORR	HF	CORR	HF	CORR	ΗF	CORR
	KaKB	14.889	14.908	2.6850	2.6858	0.5731	0.5733	0.4468	0.4472 8 9622	0.4423	0.4427 45 9986	0.3440	0.3442
m	Kg La	7.662	7.664	1.5152	1.5160	2.2231	2.2104	9.0874	8.9630	47.0695	45.9993	2.0359	2.0192
	Total	10.071	10.088	1.9051	1.9069	1.6731	1.6645	6.2072	6.1240	31.5271	30.8129	1.8460	1.8312
	KaKB	27.763	27.778	3.6824	3.6825	0.4150	0.4151	0.2330	0.2332	0.1656	0.1656	0.2466	0.2467
	KaLa	14.606	14.665	2.1449	2.1496	1.3483	1.3447	3.1670	3.1495	9.4043	9.3189	1.1615	1.1581
4	KB La	14.606	14.585	2.1449	2.1439	1.3483	1.3453	3.16/0	3776 5	9.4043 6 2247	9.3193 6 2680	1.10101	0/CL.1
	Total	18.992	19.00	4/09.2	1909.7	1.03/2	1000.1	2.1030	0//1.7	1270.0	0007.0		p
	K aK B	44.631	44.644	4.6806	4.6804	0.3252	0.3253	0.1427	0.1427	0.0790	0.0790	0.1921	0.1922
	KaLa	23.806	23.894	2.7719	2.7773	0.9809	0.9795	1.6365	1.6321	3.4424	3.4285	0.8211	0.8202
ഹ	KB La	23.806	23.759	2.7719	2.7697	0.9809	0.9799	1.6365	1.6324	3.4424	3.4287	0.8211	0.8199
	Total	30.748	30.766	3.4081	3.4091	0.7624	0.7616	1.1386	1.1358	2.3213	2.3121	0.7466	0.7455
	Rake	90 359	90.375	6.6782	6.6781	0.2269	0.2270	0.0692	0.0693	0.0266	0.0266	0.1332	0.1332
	Kala	48.962	49.113	4.0238	4.0300	0.6398	0.6393	0.6809	0.6804	0.9108	0.9104	0.5211	0.5212
2	KB La	48.962	48.860	4.0238	4.0201	0.6398	0.6396	0.6809	0.6806	0.9108	0.9105	0.5211	0.5210
	Total	62.761	62.783	4.9086	4.9094	0.5022	0.5020	0.4670	0.4767	0.6161	0.6159	0.4742	0.4741
	KaK 8	119.221	119.246	7.6775	7.6775	0.1971	0.1972	0.0522	0.0522	0.0174	0.0174	0.1155	0.1155
	KaLa	64.916	65.107	4.6493	4.6559	0.5457	0.5455	0.4924	0.4924	0.5580	0.5584	0.4412	0.4414
80	KB La	64.916	64.787	4.6493	4.6452	0.5457	0.5457	0.4924	0.4925	0.5580	0.5585	0.4412	0.4412
	Total	83.018	83.046	5.6587	5.6595	0.4295	0.4294	0.3457	0.3457	0.3778	0.3781	0.4015	0.4016
E.	ble 2.1	L.Z Exp	ectation	values	$\langle r_1^n \rangle$ and	the sta	ndard de	viation	Δr <sub>1</sub> for	the (1s	<sup>2</sup> 2s) <sup>2</sup> S st	tate for	the the
		ind	ividual	shells	and the n	ormalize	d Total	values f	or the I	i-like	ions. Tl	hese re:	sults

are derived by using Weiss<sup>(25)</sup> CI and Weiss<sup>(26)</sup> HF wavefunctions.

2	SHELL	Δτ <sub>r</sub>	Δτ <sub>1/r</sub>	۵۲ <sub>۲</sub>	۵۳ <sub>۲</sub> ,	Δτ <sub>γ</sub> .
e	KaKA	-0.06409	-0.02734	-0.04008	-0.01499	-0.04461
	KaLa	-0.00033	+0.00048	-0.00248	-0.00084	-0.00938
	KBLa	-0.00075	-0.00027	-0.00262	-0.00124	-0.01013
	Total	-0.00109	-0.01101	-0.00346	-0.00791	-0.02137
4	KαKβ	-0.04209	-0.01898	-0.03030	-0.01136	-0.03341
	KαLα	+0.00034	+0.00016	-0.00313	-0.00095	-0.00925
	KβLα	-0.00046	-0.00113	-0.00374	-0.00152	-0.01008
	Total	-0.00103	-0.00798	-0.00440	-0.00617	-0.01788
Ŋ	KaK B	-0.03083	-0.01439	-0.02435	-0.00915	-0.02672
	KaLa	+0.00061	+0.00006	-0.00301	-0.00090	-0.00813
	KBLa	-0.00032	-0.00137	-0.00379	-0.00148	-0.01005
	Total	-0.00038	-0.00623	-0.00428	-0.00504	-0.01497
2	KαKβ	-0.02028	-0.00979	-0.01742	-0.00658	-0.01904
	KαLα	+0.00046	-0.00008	-0.00252	-0.00074	-0.00628
	KβLα	-0.00049	-0.00144	-0.00335	-0.00126	-0.00807
	Total	-0.00085	-0.00439	-0.00364	-0.00368	-0.01113
ο ·	KαKβ	-0.01691	-0.00831	-0.01525	-0.00576	-0.01664
	KαLα	+0.00070	-0.00005	-0.00228	-0.00068	-0.00560
	KβLα	-0.00023	-0.00135	-0.00306	-0.00116	-0.00725
	Total	-0.00064	-0.00376	-0.00331	-0.00324	-0.00983
Tal	ble 2.1.8	The change the (1s <sup>2</sup> 2;	Δτ in the radi s) <sup>2</sup> S state fo	al and angula r the individ	r correlation ual electronic	coefficients r shells in the

like ions. The Totals for  $\Delta \tau$  were evaluated from equations (2.1.58-60) by using the normalized Totals for the appropriate values.

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N	SHELL	مر	change in <1	r <sup>n</sup> 2	5 \$	change in <	(r <sup>n</sup> )	<pre>% char</pre>	ıge in <r<sup>nr</r<sup>	2 >
		n = 1	n = 1	n = 2	n = -1	n = 1	n = 2	n = -1	n = 1	n = 2
	Ka KB	-5.127	+2.878	+4.095	+0.031	+0.032	+0.084	-2.856	-2.249	-7.582
	KaLa	+0.289	-0.475	-1.138	+0.231	-0.603	-1.382	+0.934	-0.775	-1.565
<u></u>	KB La	-0.216	-0.437	-1.116	+0.046	-0.578	-1.374	+0.091	-0.694	-1.558
	Total	-3.709	-0.124	-0.976	+0.091	-0.517	-1.340	-2.190	-0.836	-1.634
	KaKB	-3.726	+2.117	+3.072	+0.002	+0.028	+0.059	-1.986	-1.431	-4.629
- <u>-</u>	Kala	-0.037	060.0-	-0.307	+0.219	-0.266	-0.554	+0.595	-0.432	-0.828
4	KB La	-0.668	+0.012	-0.174	-0.046	-0.223	-0.537	-0.508	-0.312	-0.834
	Total	-2.680	-0.217	-0.116	+0.048	-0.207	-0.524	-1.512	-0.459	-0.903
	KaKB	-2.935	+1.670	+2.468	-0.003	+0.013	+0.032	-1.519	-1.050	-3.293
_	Kala	-0 116	+0.040	+0.022	+0.189	-0.156	-0.274	+0.430	-0.310	-0.571
<u>د</u>	KB La	-0.755	+1.139	+0.126	-0.083	-0.108	-0.254	-0.657	-0.184	-0.573
	Total	-2.105	+0.298	+0.184	+0.029	-0.105	-0.246	-1.163	-0.315	-0.628
	K ak B	-2 032	+1.172	+1.734	-0.002	+0.012	+0.016	-1.005	-0.675	-2.063
	Kala	-0.170	+0.102	+0.175	+0.155	-0.063	+0.062	+0.274	-0.195	-0.357
2	KBLa	-0.689	+0.203	+0.295	-0.089	-0.018	+0.041	-0.661	-0.080	-0.353
	Total	-1.479	+0.300	+0.325	+0.016	-0.034	-0.050	-0.793	-0.189	-0.401
	KaKb	-1.766	+1.015	+1.522	-0.006	-0.002	-0.003	-0.862	-0.585	-0.174
	ΚαΙα	-0.173	+0.119	+0.227	+0.135	-0.047	-0.008	+0.223	-0.172	-0.303
80	KB La	-0.646	+0.204	+0.323	-0.097	-0.003	+0.012	-0.647	-0.061	-0.295
	Totai	-1.572	+0.423	+0.405	+0.015	-0.014	+0.009	-0.683	-0.155	-0.338
H	ble 2.	L.9 The	percentage	change in <	r <sup>n</sup> <sub>12</sub> >, <r<sup>n<sub>1</sub>&gt;</r<sup>	and $\langle r_1^n r_2^n \rangle$	due to cori	relation fo	r the (1s <sup>2</sup> 2	s) <sup>2</sup> s state

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The HF function  $f(r_{12})$  for the  $(1s^22s)^2s$ Be<sup>+</sup>, B<sup>2+</sup>, C<sup>3+</sup>, N<sup>4+</sup> and O<sup>5+</sup> plotted against The HF Figure 2.1.1 Li, for states  $2r_{12}$  (in atomic units). (A) the KaK $\beta$ distance the scaled KaLa-shells, (C) the K $\beta$ La-shells, and (D) the shells, (B) the total distribution when normalized to unity.





Figure 2.1.2 The Coulomb holes  $\Delta f(r_{12})$  vs  $Zr_{12}$  for the  $(1s^22s)^2S$  state derived for Li, Be<sup>+</sup>, B<sup>2+</sup>, N<sup>4+</sup> and 0<sup>5+</sup>. (A) The KaKβ-shells, (B) the KaLa-shells, (C) the KβLa-shells, and (D) the total Coulomb hole for each 2 obtained here by 3 taking 1/3  $\Gamma$   $\Delta f_{ij}$   $(r_{12})$ .

For the intra-shells and the total system, the curves are ordered from right to left as Z increases.

For the inter-shells, the curves are ordered by noting that, at  $2r_{12}=5$ ,  $\Delta f(r_{12})$  decreases in value as 2 increases. At  $2r_{12}=20$ , the curves increase in value as 2 increases.



Total (-----) of these contributions is given by  $K\alpha K\beta$  +  $K\alpha L\alpha$  +  $K\beta L\alpha$ . The  $\Delta f(r_{1,2})$ -scale shells in the (1s<sup>2</sup>2s)<sup>2</sup>S state of (A) Li, (B) Be<sup>+</sup> and (C) N<sup>4+</sup>. The Sum the Sum Total Coulomb hole is the same as that for the KaKB-shell which is shown on the left of each diagram. All  $\Delta f(r_{12})$ -scale are marked in increments of 2 x Q, where Q is A comparison of the Coulomb holes vs.  $2r_{1,2}$  for the KaK $\beta$ (---given at the top of each ordinate. and KβLα (-----) Figure 2.1.3 for





Figure 2.1.5

(see over)

Eigure 2.1.5 The HF surface  $g(r_{12}, r_1)$  vs.  $(r_1^2, r_1)$  for the L1. Be<sup>+</sup> and  $N^{4+}$  in the  $(1s^22s)^2s$  state. (A) The KaKB-shells (top row), (B) the Kaka-shells (middle row) and (C) the Kulu shells (bottom row) Note that each column corresponds

to a given atom.







Figure 2.1.6

(see over)

**Figure 2.1.6** The partial Coulomb hole  $\Delta g(r_{12}, r_1)$  vs.  $(r_{12}, r_1)$  for the Li Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^2 2s)^2 s$  state. (A) the  $K\alpha K\beta$ -shells (top row), (B) the KaLa-shells (middle row) and (C) the K $\beta$ L $\alpha$ -shells (bottom row). Note that each column corresponds to a given atom.







Figure 2.1.7 (see over)

densities  $D(r_1, r_2)$  in the  $(1s^2 2s)^2 S$  state for Li, Be<sup>+</sup> and  $N^{4+}$ . (A) The KaKB-shells (top row), (B) the KaLa-shells Figure 2.1.7 A comparison of the two-particle radial (middle row), and (C) the KBLa-shells (bottom row). Note that each column corresponds to a given atom.







Figure 2.1.8

(see over)

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relative to the HF distribution, for the  $(1s^22s)^2s$  state for Li, Be<sup>+</sup> and N<sup>4+</sup>. (A) The KuKB-shells (top row), (B) the Kala-shells (middle row) and (C) the K $\beta$ La-shells (bottom **Figure 2.1.8** A comparison of the change in  $D(r_1, r_2)$ row). Note that each column corresponds to a given atom.





Bet









2.2 EXCITED STATE -  $(1s^22p)^2p$ 

#### CHAPTER 2.2.1

#### INTRODUCTION

Previously we have examined and compared the intra- and inter-shell correlation effects in position space for the ground state of Li-like ions. The analysis was performed by determining Coulomb and partial Coulomb holes and various expectation values for each electronic shell. The expectation values were used to calculate several statistical correlation coefficients  $\tau$ . The description of each individual shell, at both correlated and HF level, was obtained by partitioning the second-order density for the total system into its pair-wise components. For the intrashell, global assessments of angular and radial components of electron correlation were obtained in terms of  $\Delta \tau$  - the change in a particular  $\tau$  value when measured relative to its HF value.

In this section, the previous analysis is extended to examine the Li-like ions in the excited state  $(1s^22p)^2p$ . This state is obtained by exciting the outer electron of the  $(1s^22s)^2s$ -state into a 2p orbital and, as a consequence, it is anticipated that changes will occur in the relative importance of the correlation effects. The comparison between the correlation properties of an S-state and those of a state with angular dependence, such as a P-state, should be especially informative. The similarity and differences can be shown by comparing the behaviour of the intra- and inter-shells of the S- and P-states. The correlated wavefunctions employed throughout this work were

those of Weiss<sup>(26)</sup>, used previously by Taylor and Banyard<sup>(72)</sup> to study the correction function  $f_{i}$ , pair correlation function  $U_{ij}$  and the associated pair energies  $\epsilon_{ij}$ ; these wavefunctions have also been used by Brown and Smith<sup>(73)</sup>, Ardill and Stewart<sup>(74)</sup> and Lyons, Pu and Das<sup>(75)</sup> in the evaluation of the hyperfine structure (hfs).

The availability of extensive CI calculations by Weiss<sup>(26)</sup> for the <sup>2</sup>P state of a series of Li-like ions allows any observed change to be examined as a function of the nuclear charge Z. As before, the correlation effect can be studied by evaluating the Coulomb hole, the partial Coulomb holes and other correlation properties. When considering states of non-zero angular momentum, modifications in the evaluation of the Coulomb hole are necessary. For the inter-shells, it was also of interest to determine the  $\theta_1$ -dependent partial hole  $\Delta g(r_{12}, r_1, \theta_1)$ , where  $\theta_1$  is measured relative to the symmetry axis of the system; see for example Banyard and Reed<sup>(71)</sup>. The correlation effects in the  $K\alpha K\beta$ -shell are compared with those for the doubly-occupied K-shells in the ground states of a number of two-, three- and four-electron systems. For the <sup>2</sup>P inter-shells we are also able to compare not only with the ground state but also with the correlation effects in the 2<sup>1</sup>P and 2<sup>3</sup>P excited states of He<sup>(66)</sup>. Atomic units are used throughout this work.

Note that during the course of this work, it was reconfirmed that the correlated wavefunction of Weiss<sup>(26)</sup> for Z=8 in the <sup>2</sup>P-state of the three electron ions contains an error. Consequently this function has not been used.

# CHAPTER 2.2.2

## WAVEFUNCTIONS AND RESULTS

In the present investigation, the CI wavefunction describing the first excited <sup>2</sup>p state of the Li-like ions is again taken from the work of Weiss<sup>(26)</sup>. The procedure for analysing this wavefunction follows the same general principles as discussed when presenting equations (2.1.2-6). Briefly, each CI wavefunction for the <sup>2</sup>P state contains 45 configurations formed from a basis set  $\{\phi_1\}$  of 38 Slater type spin orbitals (STO), which extend as far as the 5g orbitals. In the basis sets  $\{\varphi_1\}$  used by Weiss<sup>(25)</sup> the functions 1s,1s'2s,2s',2p,2p',3s',3p,3p',3d,4d,4f,5d,5f and 5g were those obtained from the energy-minimization calculations for the <sup>1</sup>S ground-state of the appropriate Helike ion. Additional basis functions 1s", 2p", 2p"', and 3d' for the <sup>2</sup>P state were introduced into  $\{\varphi_1\}$  by Weiss<sup>(26)</sup> to give some description of the outer electron in the <sup>2</sup>P state. As for the <sup>2</sup>S state, all the configuration coefficients for the <sup>2</sup>P state wavefunctions were optimized, along with the orbital exponents, by using the energy variation theorem.

The un-correlated description of each ion was provided by the  $^{2}P$  restricted Hartree-Fock (RHF) wavefunction of Weiss<sup>(26)</sup>, which was constructed from a basis set containing four s-type and five p-type orbitals. This wavefunction is written as

$$\phi_{HF}(123) = (3!)^{-1/2} |\phi_{1S}^{\alpha}(1)\phi_{1S}^{\beta}(2)\phi_{2p}^{\alpha}(3)| , 2.2.1$$

where

$$\varphi_{nl} = \sum_{i=1}^{j} c_{n}^{i} \times \sum_{nl}^{i} , \qquad 2.2.2$$

and j=4 or 5 where nl = 1s or 2p, respectively. The basis functions are standard normalized STO's and are given by

$$X_{nlm}(r\theta\phi;\xi) = R_n(r;\xi)Y_{lm}(\theta,\phi) , \qquad 2.2.3$$

where

$$R_n(r;\xi) = [(2\xi)/(2n!)]^{1/2} r^{n-1} exp(-\xi r)$$
. 2.2.4

For a given HF wavefunction, Weiss minimized the total energy for all parameters including the exponents  $\xi$ .

The study of correlation properties, such as the Coulomb hole and the partial Coulomb holes, for each electronic shell requires the two-particle density to be evaluated and partitioned for both the HF and correlated wavefunctions. Following Sinanoglu, the correlated wavefunction for a Lilike ion can be expressed as

$$\Psi_{\text{corr}}(123) = \mathbf{A} \left[ \Pi(123) \left( 1 + \sum_{i=1}^{3} f_{i} / \phi_{i} + \frac{1}{\sqrt{2}} \sum_{i < j}^{3} U_{ij} / \phi_{i} \phi_{j} \right) \right]$$
  
+ 
$$\frac{1}{\sqrt{3!}} \sum_{i < j < k}^{3} U_{ijk} / \phi_{i} \phi_{j} \phi_{k} \quad ] , \qquad 2.2.5$$

where all the notation and the orthogonality conditions imposed on  $f_i$ ,  $U_{ij}$ , etc, have been defined in equations (2.1.10-20). It is to be noted that the functions  $f_i$  and  $U_{ij}$  can be obtained in a way similar to those for the  $^2s$ state by using the method of successive partial ortho-

gonalization proposed by Sinanoglu<sup>(36)</sup>. Following the procedure used in Chapter 2.1.2 (see equations (2.1.9-36)), equation (2.2.5) can be simplified to give

$$\Psi_{\text{corr}}(123) = (N!)^{-1/2} \sum_{\substack{i < j \\ i < j \\ \neq k}}^{N=3} \varepsilon_{p} \left[ A_{ij}^{12} \phi_{k}(3) + A_{ij}^{12} \phi_{k}(3) + B_{ij}^{12} \phi_{k}(3) \right]$$
  
+ $D_{ij}^{12} \phi_{k}(3) + \sqrt{2} \{ U_{ij}^{12} \phi_{k}(3) + U_{ij}^{23} \phi_{k}(1) + U_{ij}^{31} \phi_{k}(2) + \sqrt{2} \{ U_{ijk}^{12} \} \right] 2.2.6$ 

The correlated descriptions of Li, Be<sup>+</sup>, B<sup>2+</sup>, C<sup>3+</sup>, N<sup>4+</sup> and  $0^{5+}$  provided by the 45-term CI wavefunction of Weiss account for 96.0%, 90.5%, 90.1%, 88.7%, 87.7% and 87.7% of the correlation energy, respectively. The energies derived from the CI and HF wavefunctions, along with the experimental energies used in the evaluation of the correlation energy, are shown in Table 2.2.1.

Electron correlation may be investigated by examining the differences between the correlated two-particle density  $\Gamma_{\rm corr}({\bf X}_1, {\bf X}_2)$  and the corresponding HF density  $\Gamma_{\rm HF}({\bf X}_1, {\bf X}_2)$ . As in the previous section,  $\Gamma({\bf X}_1, {\bf X}_2)$  is normalized to the number of independent electron pairs within the system. The density for each individual electronic shell is obtained by partitioning  $\Gamma$  into its pair-wise components (i,j); the expressions for the HF and correlated two-particle densities have already been given in equations (2.1.41) and (2.1.43), respectively. Table 2.2.2 contains the number of CI terms which were used in the  $\Gamma_{\rm corr}({\bf X}_1, {\bf X}_2)$  for each shell. The notation used in this table has been defined in Chapter 2.1.3. In general, the partitioned expression for  $\Gamma$  can be written as

$$\Gamma(\underline{x}_{1}, \underline{x}_{2}) = \sum_{\substack{i < j} i \neq j} (\underline{x}_{1}, \underline{x}_{2}) , \qquad 2.2.7$$

where the interparticle distribution function associated with the spin orbital pair (i,j) is given by

$$f_{ij}(r_{12}) = \sum_{\substack{i < j}}^{3} \int \Gamma_{ij}(\underline{x}_{1}, \underline{x}_{2}) d\underline{x}_{1} d\underline{x}_{2} / dr_{12}$$
 2.2.8

such that, for any pair (i,j), we have

$$\int_{0}^{\infty} f(r_{12}) dr_{12} = 1 . \qquad 2.2.9$$

Calculations of  $f(r_{12})$  for non-spherically symmetric systems are complicated by the fact that the expression for  $f(r_{12})$  obtained from equation (2.2.8) will involve integrals of the most general type

$$\int Y_{1_{1}m_{1}}(1)Y_{1_{2}m_{2}}(1)Y_{1_{3}m_{3}}(2)Y_{1_{4}m_{4}}(2) dQ_{1}dX \qquad 2.2.10$$

where  $d\Omega_1$  denotes integration over angular coordinates of the position vector  $\mathbf{r}_1$ , and dX indicates integration over an angle of rotation. The general procedure for obtaining the  $f(\mathbf{r}_{12})$  distribution is outlined in the section describing the non-spherically symmetric case in Appendix A.2. The  $f_{\rm HF}(\mathbf{r}_{12})$  and the  $\Delta f(\mathbf{r}_{12})$  results are plotted against  $Zr_{12}$  in Figures 2.2.1 and 2.2.2 respectively. A comparison of the intra- and inter-shell Coulomb holes vs.  $Zr_{12}$  for Li, Be<sup>+</sup> and N<sup>4+</sup> are shown in Figures 2.2.3.

The partial Coulomb hole,  $\Delta g(r_{12}, r_1)$  characterizes the Coulomb hole when the test electron 1 is located at a

specified radial distance  $r_1$  from the nucleus. The  $g_{HF}(r_{12},r_1)$  and  $\Delta g(r_{12},r_1)$  surfaces for Li, Be<sup>+</sup> and N<sup>4+</sup> are shown in Figures 2.2.4-5. When the system possesses a natural axis of symmetry, as occurs in the P state, a partial Coulomb hole  $\Delta g(r_{12},r_1,\theta_1)$  may be defined,  $\theta_1$  being measured relative to the symmetry axis; see Appendix A.2 for the general calculation, and see also the work of Reed<sup>(77)</sup>. The partial Coulomb holes are related to  $\Delta f(r_{12})$  as follows

$$\int \Delta g(r_{12}, r_{1}, \theta_{1}) \sin \theta_{1} d\theta_{1} dr_{1} = \int \Delta g(r_{12}, r_{1}) dr_{1} = \Delta f(r_{12}) dr_{1} = \Delta f(r_{12}) dr_{1} = 2.2.11$$

For Z = 3,4 and 7, the  $g_{HF}(r_{12},r_1,\theta_1)$  and  $\Delta g(r_{12},r_1,\theta_1)$ results for the KaLa- and K $\beta$ La-shells are shown in Figures 2.2.6-9.

### One- and Two-particle expectation values

For the purposes of discussion and comparison with our work on the  ${}^{2}S$ -state, the expectation values  $\langle r_{12}^{n} \rangle$  have been evaluated using equation (2.1.49) for n = -1, 1 and 2, together with the standard deviation  $\Delta r_{12}$  defined by equation (2.1.50).

The methods used here for calculating the two-particle expectation values  $\langle (\underline{r}_1/r_1^n), (\underline{r}_2/r_2^n) \rangle$  follow those outlined previously, see equation (2.1.51). Reported in Table 2.2.3 are some two-particle expectation properties for the individual electronic shells, together with the total values for each system. The total value is given, as previously,

by  $(K\alpha K\beta + K\alpha L\alpha + K\beta L\alpha)/3$ . For the HF wavefunction, the two-particle expectation values  $\langle (\underline{r}_1/r_1^n).(\underline{r}_2/r_2^n) \rangle$  are zero for the K $\alpha K\beta$ - and K $\beta L\alpha$ -shells, so Table 2.2.4 contains the results for the K $\alpha L\alpha$ -shell only. Table 2.2.5 and 2.2.6 contain one- and two-particle radial expectation values for the HF and correlated wavefunctions. For the selected systems Li, Be<sup>+</sup> and N<sup>4+</sup>, we evaluated D<sub>HF</sub>( $r_1, r_2$ ) and  $\Delta D(r_1, r_2)$  for each electronic shell; see Figures 2.2.10-11. Figure 2.2.12 illustrates the one-particle radial density D<sub>HF</sub>( $r_1$ ) for these systems for the K $\alpha K\beta$ -, K $\alpha L\alpha$ - and K $\beta L\alpha$ shells.

As before, we assess the radial and angular components of electron correlation by evaluating various statistical correlation coefficients <sup>(68)</sup>, defined in equations (2.1.58-59). The results for  $\Delta \tau$  are presented in Table 2.2.7 and Figure 2.2.13. Table 2.2.8 contains the percentage change, due to correlation, in  $\langle r_{12}^n \rangle$ ,  $\langle r_1^n \rangle$  and  $\langle r_1^n r_2^n \rangle$  for n = -1, 1 and 2.

#### CHAPTER 2.2.3

#### DISCUSSION

The correlation properties for Li-like ions in the (1s<sup>2</sup>2p)<sup>2</sup>P state can be discussed in the same manner as for the  $(1s^22s)^2S$  state and comparisons can be made between the two states. We anticipate that the fundamental differences in correlation effects between the excited and the ground states of the ions will be associated with the differences in the symmetry of the state. For the <sup>2</sup>P state, the HF and CI energies are listed in Table 2.2.1 for  $3 \le 2 \le 8$ ; also quoted is the percentage of correlation energy accounted for in each CI wavefunction. From Table 2.2.2, it can be seen that for the <sup>2</sup>P state 41, 22 and 22 CI terms are included in the calculation of the two-particle density for the  $K_{\alpha}K_{\beta}$ -,  $K\alpha L\alpha$  - and  $K\beta L\alpha$  - shell, respectively, whereas 41, 22 and 45 CI terms were included for the <sup>2</sup>S state. Therefore, differences may be expected in the KaLa- and KBLa-shell when comparing the present results with those for the ground state.

Before the discussion of the correlation effect, it is essential to make some observations about the HF properties of the  ${}^{2}P$  state and compare them with the  ${}^{2}S$  state of the three-particle systems. Inspection of the expression for the KaK $\beta$  part of the partitioned two-particle density showed that, in its analytical form, it was identical to the K-shell description in the  ${}^{2}S$  state. This correspondence between the density expressions for the excited and ground

states also extended to the one- and two-particle radial density distributions for this shell. Therefore, the HF results for the K $\alpha$ K $\beta$ -shell in  $^2$ P are expected to be in closed agreement with those for  $^2$ S. Naturally, for the inter-shells, differences exist between  $^2$ P and  $^2$ S as a consequence of the change in symmetry of the occupied outer orbital. Such differences will be commented upon later.

## The KaKB-shell

Figure 2.2.1(A) shows Z-scaled plots of the HF interparticle distribution function  $f(r_{12})$ . The behaviour of this function is similar to those for the ground state of the Li-like ions. The K-shell curves were essentially unchanged to within graphical accuracy when compared with those in Figure 2.1.1(A). The Coulomb holes vs.  $Zr_{12}$ displayed in Figure 2.2.2(A) show a high degree of similarity at large  $Zr_{12}$  with those in <sup>2</sup>S whereas, at small  $Zr_{12}$ , these holes reveal a high degree of coincidence with respect to Z compared with those in <sup>2</sup>S. These Coulomb holes have the same shape and magnitude as those for the ground state. The radius of the <sup>2</sup>P holes decreases as Z increases and are ordered as N<sup>4+</sup> <  $c^{3+}$  <  $B^{2+}$  <  $Be^+$  < Li.

Table 2.2.3 shows the HF and correlated interparticle expectation values  $\langle r_{12}^n \rangle$ , the standard deviation  $\Delta r_{12}$  and also shows the  $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 / r_1^n r_2^n \rangle$  values for the correlated level only. The expectation values  $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 / r_1^n r_2^n \rangle$  for the correlated wavefunction in <sup>2</sup>P are greater than those in <sup>2</sup>S, except for n = 2 when Z > 5 when the converse holds. For all Z the correlation effect increases the expectation
values  $\langle r_{12}^n \rangle$  when n is positive and decreases  $\langle r_{12}^n \rangle$  when n is negative. These results are in agreement with the previous findings for the <sup>2</sup>S state of the Li-like ions, the Be-like ions<sup>(28)</sup>, and also for the He-like ions<sup>(60)</sup>.

In Figures 2.2.4(A),5(A),10(A) & 11(A) we present the  $g_{HF}(r_{12},r_1)$ ,  $\Delta g(r_{12},r_1)$ ,  $D_{HF}(r_1,r_2)$  and  $\Delta D(r_1,r_2)$  surfaces for the KaK $\beta$  shell for Li, Be<sup>+</sup> and N<sup>4+</sup>. These surfaces, as in the ground state, become less diffuse and increase in magnitude as Z increases. The general behaviour of the K-shell diagrams are comparable with the K-shell diagrams in the <sup>2</sup>S state (see Figures 2.1.6(A) - 9(A)).

Examination of the radial and angular correlation coefficients give similar trends to those found in the ground state of the Li-like ions and the results are shown in Table 2.2.7. Figure 2.2.13 shows that for  $\Delta \tau_{\gamma}$ ,  $\Delta \tau_{\gamma'}$ ,  $\Delta \tau_{\gamma''}$  and  $\Delta \tau_{1/r}$ , the variation with  $z^{-1}$  is almost linear whereas, for  $\Delta \tau_{r}$ , there is a slight curvature. Each of these quantities are greater than those in the <sup>2</sup>S state for the three-particle systems.

## The Kala- and KBLa-shells

Figures 2.2.1(B - C) show  $f_{HF}(r_{12})$  vs.  $2r_{12}$  for the KaLa- and KBLa-shells. These curves are seen to follow the same trend with respect to Z as that observed for the intershells in the ground state of the Li-like ions. The principal maximum of each  $f_{HF}(r_{12})$  refers to the most probable situation that one electron is in the K shell and

the other is in the L shell. These maxima are smaller than those of the ground state but are, of course, more diffuse. Such differences become less noticable as Z is increased. In addition, there is no mini K-shell effect in the  $f_{HF}(r_{12})$ distribution for the K $\beta$ L $\alpha$ -shell as occurred for the  $^2$ S state. The absence of this feature is due to the difference in symmetry between the K- and L-shell orbitals in  $^2$ P. The penetration of the L-shell electron into the K-shell region of the excited atom can no longer produce local regions of K $\alpha$ K $\beta$ -type symmetry.

We now examine the Coulomb holes vs.  $2r_{12}$  for the KaLaand the K $\beta$ La-shells. For Z = 3, 4 and 7, Figure 2.2.3 shows an overall similarity between the  $\Delta f(r_{12})$  characteristics of the K $\beta$ La and Kala-shells, which is in contrast to a comparison between the K $\beta$ La and KaLa curves for <sup>2</sup>S. It can be seen that the shapes of the Coulomb holes for the intershells in the <sup>2</sup>P state are less complicated than those of the inter-shell curves in <sup>2</sup>S. The holes for the intershells in <sup>2</sup>P possess a larger variation in the  $\Delta f(r_{12})$ values than that observed for the <sup>2</sup>S curves. A further point of contrast is that for the <sup>2</sup>P state, the Coulomb holes for KaLa are seen to be larger than those for K $\beta$ La. This feature was also found in the <sup>1</sup>P and <sup>3</sup>P states of He<sup>(66)</sup>. The distinction between the KaLa and K $\beta$ La curves in Figure 2.2.3 is seen to be greater for Z = 7.

An examination of the Coulomb holes for the KaLa- and K $\beta$ La- shells in <sup>2</sup>P shows that at small  $r_{12}$ , the Fermi effect in the KaLa-shell produces a vanishingly small  $\Delta f(r_{12})$ 

value, as was found for the corresponding Coulomb hole in <sup>2</sup>S. For the K $\beta$ L $\alpha$ -shell the  $\Delta f(r_{12})$ -curve indicates that there is no mini K-shell effect at small r<sub>12</sub>, in contrast to that observed in <sup>2</sup>S within the same region. In addition, Figure 2.2.3 shows that for the <sup>2</sup>P-state the  $\Delta f(r_{12})$ -values at small r<sub>12</sub> are of greater magnitude for KaLa than for K $\beta$ L $\alpha$ . This is in contrast with the He work <sup>(66)</sup> for <sup>1</sup>P and <sup>3</sup>P. This becomes more understandable when we compare the magnitude of  $f(r_{12})$  at small  $r_{12}$  for both the HF and correlated description for each shell. As might be expected, due to the Fermi effect, the  $f(r_{12})$  for the KaLa-shell gives a flat region at small  $r_{12}$  at both HF and correlated levels. On the other hand, the HF and correlated results for the KBLa-shell do not exhibit a flat regions and, further, we also note that, for each description,  $f(r_{12})(KaLa) < f(r_{12})(K\beta La)$  when  $r_{12}$  is small. However, since  $f(r_{12})$  for K La at both the HF and correlated levels are of similar magnitude, the  $\Delta f(r_{12})$  values are exceedingly small. For the KaLa-shell, although the individual  $f(r_{12})$ values are very small, the resulting  $\Delta f(r_{12})$  is, in fact, somewhat larger than that for the  $K\beta L\alpha$  shell as shown in Figure 2.2.3.

The  $g_{HF}(r_{12},r_1)$  and  $\Delta g(r_{12},r_1)$  surfaces for the KaLaand K $\beta$ La-shells of Li, Be<sup>+</sup> and N<sup>4+</sup> are shown in Figures 2.2.4(B - C) and 2.2.5(B - C), respectively. As in the <sup>2</sup>S state, the  $g_{HF}(r_{12},r_1)$  densities for the KaLa- and K $\beta$ Lashells show the same characteristics in the region of the diagonal  $r_{12} = r_1$  axis, when  $r_1$  is large compared with  $r_K$ . This similarity also holds for the features parallel to the

 $r_{12}$  axis, when  $r_{12} > r_1 = r_K$ . However, when  $r_{12} = r_1 \approx r_K$ the  $g_{HF}(r_{12},r_1)$  surface for K $\beta$ L $\alpha$ -shell shows a mini K-shell density in <sup>2</sup>S, whereas this density does not appear in the  $g_{HF}(r_{12},r_1)$  surface for the K $\beta$ L $\alpha$ -shell in <sup>2</sup>P due to the different symmetry.

The influence of electron correlation on the  $g(r_{12}, r_1)$ densities in the <sup>2</sup>P state is shown for Z = 3, 4 and 7 in Figures 2.2.5(B - C). We see from the  $\Delta g(r_{12}, r_1)$  diagrams that when the test electron is in the L-shell i.e.  $r_1 \approx r_{T_1}$ , a localized positive region exists either side of the  $r_{12}$  = r, diagonal. This is in contrast with the corresponding diagrams for <sup>2</sup>S of Li-like ions and also in contrast with He work<sup>(66)</sup>. Banyard and Youngman<sup>(66)</sup> established that the for the <sup>1</sup>S, <sup>3</sup>S, <sup>1</sup>P and <sup>3</sup>P states, the  $\Delta g(r_{12}, r_1)$  surfaces show a negative region on the near side of the nucleus  $(r_{12})$  $\langle r_1 \rangle$  and a positive region on the far side  $(r_{12} > r_1)$ , with respect to the position of the test electron. The reason for this contrast might be due to the form of the CI wavefunction<sup>(26)</sup> for the <sup>2</sup>P state. Analysis shows that for the <sup>2</sup>P wavefunction of Weiss, radial correlation is dominant when considering the KL inter-shells. Therefore, any correlation induced change in an angular property such as <cosy>, for instance, is expected to be much smaller than that for the inter-shells in <sup>2</sup>S. When comparing these values for the KaLa-shell it is found that  $\Delta \tau_{\gamma^{H}}$  (= $\Delta \langle \cos \gamma \rangle$ ) in <sup>2</sup>P is only one-third of that for KaLa in the <sup>2</sup>S state of Li, whereas for the  $K\beta L\alpha$ -shell the ratio is about onequarter.

Clearly, from the viewpoint of using the change in (COSY) as some rough measure of angular correlation, we see from Table 2.2.3 and 2.2.7 that the angular effect in the  $^{2}P$ inter-shell descriptions is quite small. Indeed, for Li, the values of  $\Delta \tau_{\chi H}$  for KaLa and KBLa are only -0.00328 and -0.00229, respectively. Even so, the small difference between these inter-shell values does seem to show itself in the contour diagrams for the partial Coulomb holes (these contour diagrams are not presented here for reasons of space). When  $r_1 \approx r_L$ , both inter-shells appear, on first inspection, to be symmetric in their positive accumulation about the  $r_{12} = r_1$  diagonal axis. However, closer examination reveals that the KaLa accumulation has a slightly higher asymmetry than that observed for the  $K\beta L\alpha$  shell. This is in keeping with relative magnitudes of the  $\Delta \tau_{s}$ . values for the inter-shells given above.

All the above observations seem to be in agreement with the conclusions of Smith and  $Brown^{(78)}$  that configurations of the type spd, sdf, etc. have not been introduced into the  $^{2}p$  wavefunction. Such configurations would provide a specific introduction of angular correlation between the outer and inner electrons. Thus, in the Weiss wavefunction analysed here, any angular effect seems to be of a secondary nature and is an indirect consequence of introducing <u>radial</u> correlation into an inter-shell of P symmetry.

Returning to the partial Coulomb holes, let us now consider the behaviour of the Li  $\Delta g$ -surface when  $r_1 \approx r_K$ . This partial hole shows that as  $r_{12}$  decreases from a large

value,  $\Delta g$  changes from being negative to positive. This behaviour indicates that the probability density has moved inwards from the outer regions of the L shell. We also note that this negative region, which is parallel to the r<sub>12</sub> axis, is more diffuse than that of the <sup>2</sup>S at large r<sub>12</sub> values. This is in keeping with the fact that in the D<sub>HF</sub>(r<sub>1</sub>) vs. r<sub>1</sub> curve for <sup>2</sup>P the L shell maximum is located at 3.80, compared with the L shell maximum at 3.10 for the D<sub>HF</sub>(r<sub>1</sub>) vs. r<sub>1</sub> curve for the <sup>2</sup>S state.

For the <sup>2</sup>P state of the Li-like ions, we can discuss the functions  $g(r_{12}, r_1, \theta_1)$  and  $\Delta g(r_{12}, r_1, \theta_1)$ , since an angle  $\theta_1$ can be measured relative to the symmetry axis of the state of the system. For the KaLa- and K $\beta$ La-shells Figures 2.2.6 - 7 show the change in the structure of the  $g_{\rm HF}(r_{12}, r_1, \theta_1)$ surface with respect to  $\theta_1$  for Li, Be<sup>+</sup> and N<sup>4+</sup>. When  $\theta_1 =$ 90°, the test electron will be located in the nodal plane of the p orbital and hence refers only to the K-shell. Consequently there is no diagonal feature when  $r_1$  is large. When  $r_1$  is small, the test electron is located in the Kshell and the  $g_{\rm HF}(r_{12}, r_1, \theta_1 = 90^\circ)$  surface reveals a parallel effect.

Consider now the  $g_{HF}(r_{12},r_1,\theta_1)$  surface when  $\theta_1 = 0^{\circ}$ . At this angle the test electron must be along the unique line which is perpendicular to the nodal plane. Thus the test electron can be in the K-shell or in the L-shell, and the  $g_{HF}(r_{12},r_1,\theta_1=0^{\circ})$  surface for the inter-shells possesses both diagonal and parallel features. In this case the diagonal feature seems more significant than the parallel one.

For  $\theta_1 = 30^\circ$ , 60° and 90°, the  $g_{HF}$  surfaces reveal the changes in the relative magnitudes of the diagonal and parallel features which occur as  $\theta_1$  becomes larger. This trend is a result of the decreasing radial overlap between the s and p orbitals as  $\theta_1$  is increased. Consider the  $\Delta g(r_{12}, r_1, \theta_1)$  in Figures 2.2.8 - 9 for the inter-shells when 2 = 3, 4 and 7. For  $\theta_1 = 90^\circ$ , the  $\Delta g(r_{12}, r_1, \theta_1)$  behaves like the parallel feature seen in the angularly-integrated  $\Delta g(r_{12}, r_1)$ -surface; as  $r_{12}$  increases, the parallel feature is seen to change sign from negative to positive and back to negative. When  $\theta_1 = 0^{\circ}$ ,  $\Delta g(r_{12}, r_1, \theta_1)$  now behaves like  $\Delta g(r_{12}, r_1)$  along the diagonal. As  $\theta_1$  increases from 0° to 90°, the parallel feature in  $\Delta g(r_{12}, r_1, \theta_1)$  gets emphasized whereas the diagonal feature is reduced. In general, we note that when  $\theta_1 = 60^{\circ}$  the  $\Delta g(r_{12}, r_1, \theta_1)$  surface has characteristics which are very much like those of the integrated  $\Delta g(r_{12}, r_1)$  surface. The above behaviour holds for Li, Be<sup>+</sup> and N<sup>4+</sup> and only the scales and magnitudes will change. The comparison between the KaLa- and KBLa-diagrams for  $\Delta g(r_{12}, r_1, \theta_1)$  reveals that we get similar features except that at small  $r_{12}$  and small  $r_1$  we find that  $\Delta g(K \alpha L \alpha)$ >  $\Delta g(K\beta L\alpha)$ . Naturally, this difference is also evident in the angularly-integrated holes shown in Figures 2.2.5(B -C).

Let us now examine the  $D(r_1, r_2)$  surfaces for the intershells at the HF level of description. Figures 2.2.10(B -C) show the  $D_{HF}(r_1, r_2)$  densities for KaLa and KBLa for Li, Be<sup>+</sup> and N<sup>4+</sup>. These probability densities indicate that when

one electron is near the nucleus, the other is further away.

For a given atom the  $D_{\rm HF}(r_1,r_2)$  for the KaLa-shell is equal to that for the K $\beta$ La-shell in the  $^2P$  state whereas, in  $^2$ S, these densities are not equal due to the presence of the Fermi effect in the KaLa-shell and the occurrence of the mini K-shell density in the K $\beta$ La-shell. This difference in the  $^2$ S arises from the existence of the cross term in the  $D_{\rm HF}(r_1,r_2)$ -expression for the KaLa-shell. In contrast, for  $^2P$ , angular integration removes the cross-term when determining  $D_{\rm HF}(r_1,r_2)$  for the KaLa-shell due to the angular orthogonality between the 1s and 2p orbitals.

Due to the difference in symmetry for the inter-shell orbitals in <sup>2</sup>P compared with <sup>2</sup>S, we note that the uncorrelated two-particle radial density  $D_{HF}(r_1, r_2)$  will be more diffuse in the <sup>2</sup>P state than in the <sup>2</sup>S state. As in <sup>2</sup>S, the  $D_{HF}(r_1, r_2)$  distribution for the excited state of the Li-like ions becomes less diffuse and increases in magnitude as Z increases. Having discussed the  $D_{HF}(r_1, r_2)$  properties, let us consider the influence of correlation on these radial distributions (see Figures 2.2.11(B - C)) and on the related expectation values  $\langle r_1^n r_2^n \rangle$ , (see Table 2.2.6). For Li, Be<sup>+</sup> and  $N^{4+}$ , the  $\Delta D(r_1, r_2)$ -surfaces show that the correlation effects are very similar for both the KaLa- and K $\beta$ La-shells. Therefore, the  $\Delta D(r_1, r_2)$  surfaces for the KaLa-shell reveal the same characteristics as those for the  $K\beta L\alpha$ -shell, but the magnitudes of these features are greater in KaLa than that in K<sub>β</sub>L<sub>α</sub>. In contrast, for the <sup>2</sup>S state, the  $\Delta D(r_1, r_2)$ surfaces show that the correlation effects are not the same

for both shells due to the existence of the mini K-shell in the K $\beta$ L $\alpha$  diagram and the presence of the Fermi effect in the K $\alpha$ L $\alpha$ . In addition to that, the  $\Delta D(r_1, r_2)$  density in the <sup>2</sup>S state for the K $\alpha$ L $\alpha$ -shell seems smaller than that for K $\beta$ L $\alpha$ . In general, the comparison in magnitude of the  $\Delta D(r_1, r_2)$ density between the K $\alpha$ L $\alpha$ - and K $\beta$ L $\alpha$ -shells in the <sup>2</sup>P and <sup>2</sup>S states follows the comparison of the  $\Delta f(r_{12})$  values in both <sup>2</sup>P and <sup>2</sup>S states. A summary of the percentage changes in the one- and two-particle expectation values (see Tables 2.2.5 and 2.2.6, respectively) is presented in Table 2.2.8.

## CHAPTER 2.2.4

## SUMMARY

An examination of electron correlation in the  $^{2}P$  excited state of the three-electron ions shows that the results obtained for the K-shell are quite similar to those for the K-shell in ground state. For the KaLa- and K $\beta$ La-shells, the results illustrate that marked differences exist between the excited and ground states as a consequence of the change in symmetry.

The Coulomb holes for the K-shell of the three-electron series possess considerable similarity when plotted against the scaled coordinate  $2r_{12}$ . As a consequence of the difference between the symmetry of the occupied outer orbital between the inter-shells for <sup>2</sup>p and <sup>2</sup>S, we found that the shape of the  $\Delta f(r_{12})$  curves for the inter-shells in the <sup>2</sup>P state is less complicated than that for the intershell curves in <sup>2</sup>S. In addition, the Coulomb holes show an overall similarity for the KaLa- and KBLa-shells, and this in contrast to the comparison between these shells for is the <sup>2</sup>S state. For Z = 3, 4 and 7, the ordering of the KaLaand K $\beta$ L $\alpha$  Coulomb holes follows that of the <sup>1</sup>P and <sup>3</sup>P states He. For example, for the excited states of He, Banyard of and Youngman<sup>(66)</sup> found that, for P symmetry, the Coulomb holes for the triplet are larger in their  $\Delta f(r_{12})$  values than those for the singlet state.

For the <sup>2</sup>P-state of the Li-like ions, the Coulomb hole for the whole atom showed that, when  $Zr_{12} < 5$ , the characteristics were the same as those for the K $\alpha$ K $\beta$  Coulomb hole; this feature also occurred in our earlier examination of the <sup>2</sup>S state. When  $Zr_{12} > 5$ , the total holes for the <sup>2</sup>P state differ in character from those for <sup>2</sup>S. This is attributable to differences which arise between the sets of Coulomb holes for the inter-shells. Such differences are a consequence of the change in symmetry of the orbital description of the outer electron.

The use of the partial Coulomb holes allowed us to examine the Coulomb hole as a function of the location of the test electron. For the KaK<sub>β</sub>-shell, the  $\Delta g(r_{12}, r_1)$ surface shows characteristics almost identical with those seen for the ground state. For the inter-shells, the  $\Delta g(r_{12}, r_1)$  surfaces showed a feature which was not present for those obtained in <sup>2</sup>S. This feature, which occurred on the diagonal axis when  $r_1 \approx r_{12}$  for both KaLa- and K $\beta$ Lashells, is due to the way in which Weiss<sup>(26)</sup> constructed the CI wavefunction for the <sup>2</sup>P state. The absence of the configurations of the type spd, sdf,  $d^2f$  etc. from the CI wavefunction implies that no specific angular correlation has been introduced into the description of the intershells. Consequently, the behaviour of the partial Coulomb holes when  $r_1 \approx r_L$  is governed by radial correlation. This was supported by the inspection of the magnitude of  $\Delta \tau_{\mu}$  $(=\Delta(\cos\gamma))$  which, for the inter-shells, was found to be only less, of the value obtained for the corresone-third, or ponding shells in the <sup>2</sup>S state of Li. This finding

illustrates that the present mode of analysis is also capable of indicating the weakness of a wavefunction. The partial Coulomb holes  $\Delta g(r_{12}, r_1, \theta_1)$  for the inter-shells gave further insight into the structure of the corresponding angularly integrated hole  $\Delta g(r_{12}, r_1)$ .

The two-particle radial density  $D_{HF}(r_1,r_2)$  and the density difference  $\Delta D(r_1, r_2)$  for the KaK $\beta$  in the <sup>2</sup>P state features similar to those obtained for the showed corresponding density in <sup>2</sup>S. Correlation reduces the twoparticle radial density along the  $r_1 = r_2$  axis, where it is a maximum, and increases the density in the off-diagonal regions. This behaviour holds for Li, Be<sup>+</sup> and N<sup>4+</sup> for the KaK $\beta$  shell. As Z increases, the  $D_{HF}(r_1, r_2)$  and  $\Delta D(r_1, r_2)$ densities increase in magnitude and become less diffuse. For the inter-shells the  $D_{HF}(r_1, r_2)$  and  $\Delta D(r_1, r_2)$  surfaces show a high degree of similarity between the KaLa- and K $\beta$ Lashells for a given atom and also show that the changes in the two-particle radial density are greater in magnitude for the KaLa than those for the K $\beta$ La. By contrast, in the <sup>2</sup>Sstate the  $D_{HF}(r_1, r_2)$  and the  $\Delta D(r_1, r_2)$ -surfaces reveal a distinction between the KaLa- and KBLa-diagrams and also show that  $\Delta D(r_1, r_2)$  for KaLa is smaller in magnitude than  $\Delta D(r_1, r_2)$  for K  $\beta La$ . This contrast seems not surprising in view of the presence of Fermi correlation in the KaLa-shell of the  $^{2}P-$  and  $^{2}S-$ states.

Tables and Figures - Part 2.2

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ap integrals	es and overla	cion energie	and correlat	energies	Wavefunction	<b>Table 2.2.1</b>
1.045375	0.999693	0.999504	0.999347	0.998907	0.998242	<pre></pre>
87.7	87.7	88.7	1.06	90.5	96.0	<b>LE</b> COLL
63.78971	48.01055	34.48193	23.20442	14.17932	7.41016	Experimental
63.78314	48.00411	34.47597	23.19936	14.17466	7.40838	Correlated
63.73666	47.95775	34.42986	23.15370	14.13085	7.36507	HF
8	7	و	S	4	£	2

lation energies and overlap integrals	wavefunctions. Note that all energies	in Atomic Units. The percentage	$\mathbf{E}_{\mathbf{corr}} = 100 \left( \mathbf{E}_{\mathbf{corr}} - \mathbf{E}_{\mathbf{HF}} \right) / \left( \mathbf{E}_{\mathbf{exp}} - \mathbf{E}_{\mathbf{HF}} \right).$	
and corr	ind HF <sup>(26)</sup>	expresse	fined as	
energies	ated <sup>(26)</sup>	and are	lergy is de	
vefunction	tween correl	te negative	rrelation er	
1 Wa	þe	aı	0 0	

	Number al	ld type of	correlatio	n configur	ations con	sidered pe	r shell
ЗНЕГГ	(ss) <sup>1</sup> Sp	(pp) <sup>1</sup> sp	(dd) <sup>1</sup> sp	(ff) <sup>1</sup> sp	(99) <sup>1</sup> Sp	(ss) <sup>3</sup> Sp	(dd) <sup>3</sup> sp
Κα Κβ	19	11	L	3	t	0	0
Κα Γα	19	0	0	ο	0	3	0
ΚβΙα	19	0	0	ο	0	3	0

type A summary of the correlation configurations and considered in the two-particle density for each shell. Table 2.2.2

	$\langle (\mathbf{r}_1/\mathbf{r}_1) \cdot (\mathbf{r}_2/\mathbf{r}_2) \rangle$		$\langle r_{12}^n \rangle$		Δr <sub>12</sub>
Z SHELI	L n = 2 n = 1 n = 0	n = -1	n = 1	n = 2	
	CORR CORR CORR	HF CORR	HF CORR	HF CORR	HF CORR
ΚαΚβ Καία 3 Κβία	224980453501834 009970098601854 001510453501834	1.64962 1.56399 0.26120 0.26060 0.26416 0.26416	0.83985 0.86423 4.83919 4.82052 4.83374 4.81079	0.89459 0.9310 28.26402 27.9225 28.24206 27.8519	8 0.43502 0.42917 7 2.20143 2.16452 2 2.20839 2.16985
Tota	1078820335201841	0.72499 0.69625	3.50426 3.49851	19.13355 18.9016	6 2.61796 2.58114
ΚαΚβ Καία 4 Κβία	315930343200764 060400261302079 004260032400356	2.27067 2.18338 0.51737 0.51364 0.53181 0.52955	0.60806 0.62145 2.42223 2.43587 2.41016 2.42092	0.46760 0.4826 7.06115 7.1323 7.02870 7.089	2 0.31282 0.31053 3 1.09269 1.09493 1 1.10446 1.10827
Tota	1126860212301066	1.10662 1.07552	1.81348 1.82608	4.85248 4.901	1.25051 1.25171
ΚαΚβ ΚαΙα 5 <b>ΚβΙα</b>	404110275200404 154110374101650 006970031100193	2.89190 2.80481 0.76035 0.75737 0.79049 0.78975	0.47664 0.48459 1.63662 1.64003 1.61862 1.61962	0.28696 0.2935 3.21097 3.2208 3.15861 3.1609	9 0.24450 0.24240 6 0.72968 0.72882 4 0.73394 0.73334
Tota	1188400226800749	1.48091 1.45064	1.24396 1.24808	2.21884 2.225	13 0.81939 0.81696
KaKß KaLa 6 KbLa	490080229400246 288510448801261 009550027800111	3.51448 3.42737 0.99672 0.99425 1.04211 1.04252	0.39168 0.39704 1.24249 1.24269 1.22863 1.22625	0.19355 0.1972 1.84491 1.8425 1.82265 1.8116	22 0.20035 0.19895 33 0.54875 0.54611 55 0.55958 0.55496
Tota	1262710235300539	1.85110 1.82138	0.95427 0.95533	1.28703 1.2836	0 0.61351 0.60922
ΚαΚβ Καία 7 κβία	577700196900165 462380500400976 012030024600068	4.13773 4.05068 1.22958 1.22707 1.29150 1.29181	0.33236 0.33618 1.00382 1.00345 0.99059 0.98904	0.13925 0.1414 1.20145 1.1982 1.18367 1.1784	12 0.16965 0.16853 7 0.44021 0.43744 17 0.44989 0.44752
Tota	1350700240600403	2.21960 2.18985	0.77559 0.77622	0.84146 0.8393	19 0.48982 0.48670
Table	2.2.3 Some two-particle	expectation prop	erties for the	<pre>(1s<sup>2</sup>2p)<sup>2</sup>p state 1</pre>	or the individual
	shells and the	normalized Total	values for the	e Li-like ions.	These results are
	derived by using W	eiss <sup>(26)</sup> CI and W	leiss <sup>(26)</sup> HF Vave	efunctions.	

8	< (E <sup>1</sup> / I	$r_{1}^{n}$ ) ( $r_{2}$ / $r_{3}^{n}$ ) >	
	n = 2	и н - н и	0 = u
m	0.0077	-0.0066	-0.0108
4	0.0544	-0.02152	-0.0160
0 1	).1447	-0.0330	-0.0140
9	0.2763	-0.0409	-0.0112
0	0.4480	-0.0466	-0.0089

Table 2.2.4 Values of  $\langle (\mathbf{r}_{1}, \mathbf{r}_{1}^{n}), (\mathbf{r}_{2}, \mathbf{r}_{2}^{n}) \rangle$ , when n=2,1 and 0, at HF level for the KaLa-shell in Li-like ions. The results for the  $K\alpha K\beta$  - and  $K\beta L\alpha$  -shells are zero.

							~	rn >				۵r	
2	ITIHS	" "	-2	u		<b>n</b>		" 2	- 2	" ג	= 3		<u> </u>
		HF	CORR	HF	CORR	HF	CORR	HF	CORR	HF	CORR	ΗF	CORR
e	KaKp KaLa KpLa Total	14.8903 7.4938 7.4938 9.9593	14.9147 7.5155 7.4963 9.9755	2.6850 1.4750 1.4750 1.8783	2.6865 1.4769 1.4747 1.8794	0.5733 2.6844 2.6844 1.9807	0.5733 2.6734 2.6740 1.9736	0.4473 14.1341 14.1341 14.1341 9.5710	0.4473 13.9590 13.9603 9.4556	0.4434 94.7915 94.7915 94.7915 63.3421	0.4433 92.5747 92.5771 92.5771 61.8650	0.3 <b>444</b> 0 2.6321 2 2.6321 2 2.6321 2 2.3767 2	.3445 .6100 .6096 .3581
4	KαKβ KαLα KβLα Total	27.7325 14.0644 14.0644 18.6205	27.7556 14.1195 14.0306 18.6352	3.6793 2.1079 2.1079 2.1079 2.6317	3.6802 2.1111 2.1041 2.6318	0.4157 1.3923 1.3923 1.3928	0.4157 1.3968 1.3980 1.0702	0.2340 3.5159 3.5159 2.4220	0.2341 3.5442 3.5458 3.5458 2.4414	0.1670 11.5331 11.5331 7.7444	0.1671 11.6631 11.6651 7.8317	0.2475 0 1.2559 1 1.2559 1 1.1331 1	.2476 .2622 .2615 .1385
ß	KaK KaLa KBLa Total	<b>44</b> .5577 22.7168 22.7168 22.99971	44.5778 22.8049 22.6469 30.0098	4.6748 2.7375 2.7375 2.7375 3.3833	<b>4</b> .6755 2.7427 2.7328 3.3837	0.3259 0.9554 0.9554 0.7456	0.3260 0.9553 0.9563 0.7459	0.1434 1.5915 1.5915 1.5915	0.1435 1.5931 1.5941 1.1102	0.0798 3.4580 3.4580 2.3319	0.0799 3.4652 3.4662 3.4662 2.3371	0.1930 0 0.8239 0 0.8239 0 0.8239 0	. 1931 . 8249 . 8244 . 7443
ى	KaKβ KaLa KβLa Total	65.3773 ( 33.4519 : 33.4519 : 33.4519 : 44.0937 •	65.3939 33.5679 33.3509 44.1043	5.6717 3.3653 3.3653 3.3653 4.1341	75.6722 3.3716 3.3604 13.3604	0.2679 0.7314 0.7314 0.5769	0.2680 0.7302 0.7309 0.5764	0.0967 0.9113 0.9113 0.6398	0.0968 0.9082 0.9088 0.6379	0.0441 1.4828 1.4828 1.4828	0.0442 1.4746 1.4752 0.9980	0.1580 0 0.6135 0 0.6135 0 0.6135 0	. 1581 . 6124 . 6120 . 5529
7	KαKβ KαLα KβLα Total	90.1942 46.2696 46.2696 46.2696	90.2042 46.4080 46.1399 50.9174	6.6694 3.9921 3.9921 4.8845	t 6.6697 3.9988 3.9869 3.9869	0.2274 0.5940 0.5940 0.4718	0.2275 0.5928 0.5934 0.4712	0.0696 0.5918 0.5918 0.5918	0.0697 0.5891 0.5895 0.4161	0.0269 0.7702 0.7702 0.5224	0.0268 0.7639 0.7642 0.7642	0.1338 0 0.4889 0 0.4889 0 0.4418 0	.1338 .4875 .4872 .4872
Tab	le 2.2.5	Expectat individu	tion va Lal sha	alues ells a	$\langle r_1^n \rangle$ a ind the	nd the norma	stand. 1ized	ard dev Total va	riation / Nue for	)r <sub>1</sub> for t the Li-]	the (1s <sup>2</sup> ; Like ion:	2p) <sup>2</sup> p sta <sup>.</sup> s. The r	te for tesults

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derived by using Weiss<sup>(26)</sup> CI and Weiss<sup>(26)</sup> HF wavefunctions.

						$\langle r_1^n r_1 \rangle$	n > 2				
2	SHELL	" "	2	= u	-	" 2	1	" "	2	"u	e
		HF	CORR	HF	CORR	HF	CORR	HF	CORR	HF	CORR
	Ka KB	221.7224	193.4160	7.2090	6.9985	0.3287	0.3202	0.2001	0.1814	0.1966	0.1592
	KaLa	1.4475	1.4166	0.7116	0.7092	2.7493	2.7346	12.4443	12.2407	83.8582	81.1765
m	KB La	1.4475	1.4436	0.7116	0.7122	2.7493	2.7322	12.4443	12.2313	83.8582	81.1353
	Total	74.8725	65.4253	2.8774	2.8066	1.9424	1.9290	8.3629	8.2178	55.9710	54.1570
	K αK B	769,0927	697 7410	13 5369	13 2525	0 1728	0 1697	O OFAR	0 0510	0 0207	
	Kala	10 9952	10 6707	1 9744		0 9847			100.0	2 2 2 2 2 2	1420.0
4	KBLa	10.9952	10.9030	1.9744	1.9692	0.9847	0.9850	1.5913	1.5869	3.8245	3.7820
	Total	263.6930	239.7728	5.8286	5.7257	0.7141	0.7142	1.7092	1.0771	2.5590	2.5342
	KaKB	1985.3853	1840.5187	21.8539	21 4955	0 1062	0 1048	0 0206	0 0195	0 0064	0 0057
	KaLa	39.0194	38.1017	3.7405	3.7167	0.5166	0.5165	0.4361	2554 0	0.5458	0 5369
S	KB La	39.0194	38.8134	3.7405	3.7419	0.5166	0.5145	0.4361	0.4311	0.5458	0.5330
	Total	687.8114	639.1415	9.7784	9.6514	0.3798	0.3786	0.2976	0.2948	0.3660	0.3585
	KaKB	4274.1903	4017.1976	32.1678	31.7352	0.0718	0.0710	0.0094	0600.0	0.0019	0.0018
	Ka La	99.7905	97.7746	6.0057	5.9773	0.3202	0.3196	0.1670	0.1655	0.1289	0.1261
9	KB La	99.7905	99.3249	6.0057	6.0130	0.3202	0.3184	0.1670	0.1644	0.1289	0.1250
	Total	1491.2581	1404.7648	14.7264	14.5751	0.2374	0.2363	0.1145	0.1130	0.0866	0.0843
	KaKB	8134.9974	7718.4913	44.4804	43.9729	0.0517	0.0512	0.0048	0.0047	0.0007	0.0006
1	KaLa	211.5831	207.7044	8.7697	8.7336	0.2185	0.2180	0.0776	0.0769	0.0407	0.0398
2	KB La	211.5831	210.5467	8.7697	8.7791	0.2185	0.2172	0.0776	0.0763	0.0407	0.0394
	Total	2852.6879	2712.2791	20.6731	20.4954	0.1629	0.1622	0.0533	0.0526	0.0273	0.0266
Tab	le 2.2	.6 Expecta	tion value:	$z \langle r_{1}^{n} r_{2}^{n} \rangle$	for the th	ie (1s <sup>2</sup> 2p)	<sup>2</sup> P state	for the :	individua	l shells (	and the
		normali	ized Total	values	for the	Li-like	ions.	The resi	ults are (	derived by	y using
		Weiss <sup>(2</sup>	26) CI and V	Weiss <sup>(26)</sup>	HF wavefu	inction.					

2	SHELL	Δτ <sub>r</sub>	Δτ <sub>1/r</sub>	Δτ <sub>γ</sub>	Δτ <sub>γ</sub> ,	Δτ <sub>γ</sub>	\$
e	KαKβ	-0.07125	-0.02839	-0.04099	-0.01508	-0.04535	3.0582
	KαLα	-0.00445	-0.00065	-0.00056	-0.00030	-0.00328	0.7150
	KβLα	-0.00555	+0.00044	-0.00040	-0.00020	-0.00229	0.6266
	Total	-0.00290	-0.01139	-0.00112	-0.00746	-0.01697	1.3731
4	KaK8	-0.05115	-0.02052	-0.03264	-0.01138	-0.03432	2.2686
	KaLa	+0.00002	-0.00225	-0.00131	-0.00041	-0.00461	0.5307
	KBLa	-0.00444	+0.00069	-0.00101	-0.00030	-0.00324	0.4493
	Total	-0.00244	-0.00871	-0.00216	-0.00583	-0.01406	0.9212
ß	KαKβ	-0.03989	-0.01607	-0.02814	-0.00907	-0.02752	1.8057
	KαLα	+0.00150	-0.00248	-0.00158	-0.00039	-0.00446	0.2449
	KβLα	-0.00487	+0.00105	-0.00121	-0.00031	-0.00311	0.0881
	Total	-0.00239	-0.00695	-0.00255	-0.00031	-0.01170	0.6159
و	KαKβ	-0.03269	-0.01320	-0.02542	-0.00749	-0.02294	1.4873
	KαLα	+0.00117	-0.00241	-0.00162	-0.00034	-0.00398	0.3093
	KβLα	-0.00579	+0.00108	-0.00122	-0.00029	-0.00278	0.1434
	Total	-0.00263	-0.00578	-0.00263	-0.00387	-0.01001	0.5708
~	ΚαΚβ	-0.02768	-0.01120	-0.02362	-0.00640	-0.01969	1.2635
	Καία	+0.00075	-0.00228	-0.00155	-0.00028	-0.00347	0.3057
	Κβία	-0.00612	+0.00099	-0.00115	-0.00026	-0.00246	0.1866
	Τοtal	-0.00268	-0.00496	-0.00259	-0.00026	-0.00854	0.5218
Ial	b <b>le 2.2.7</b>	The chang Also lis function Were eva	ge <b>Ar in the</b> ted is the f <sub>HF</sub> (r <sub>12</sub> ) wh luated from e	radial and a percentage nich has been equations (2.	ngular corre of the inte redistribut 1.58 - 60) b	lation coeff rparticle di ed. The Tot y using the	ficients τ. Istribution cals for Δτ normalized

totals for the appropriate expectation values.

for	lation	to correl	$ r_2^n\rangle$ due	and $\langle \mathbf{r}_{1}^{\mathbf{r}}$	2 <sup>2</sup> , <r<sup>n/<sub>1</sub></r<sup>	ie in <r<sup>n</r<sup>	je chang	percentaç	I The I	ole 2.2.6	Ta
98	-1.2	-0.442	-0.860	-0.408	-0.124	+0.013	-0.246	+0.081	-1.340	Total	
75	-1.5	-0.566	+0.107	-0.399	-0.101	-0.130	-0.439	-0.157	+0.241	KB La	2
37	-0.8	-0.917	-0.412	-0.469	-0.197	+0.167	-0.264	-0.037	-0.205	KaLa	
27	-3.4	-0.944	-1.141	+0.035	+0.007	+0.005	+1.560	+1.148	-2.104	KaKB	
<b>05</b>	-1.3(	-0.448	-1.027	-0.294	-0.097	+0.015	-0.144	+0.111	-1.606	Total	
96	-1.5(	-0.568	+0.121	-0.276	-0.065	-0.146	-0.603	-0.194	+0.039	KBLa	9
87	-0.8	-0.176	-0.474	-0.346	-0.167	+0.188	-0.129	+0.016	-0.248	KaLa	
92	-4.0	-1.125	-1.345	+0.031	+0.007	+0.009	+1.897	+1.370	-2.479	KaKB	
50	-0.9	-0.314	-1.299	+0.124	+0.039	+0.012	+0.283	+0.331	-2.044	Total	
53	-1.1	-0.395	+0.038	+0.160	+0.095	-0.170	+0.074	+0.061	-0.093	KBLa	ŝ
20	-0.5	-0.012	-0.636	+0.096	-0.007	+0.191	+0.308	+0.208	-0.392	KaLa	
5	- 1 0 0	-1 388	-1.640	+0.026	+0,006	+0.015	+2.310	+1.669	-3.012	K aK B	
93	-0.1	+0.018	-1.764	+0.802	+0.320	+0.004	+1.007	+0.695	-2.810	Total	
78	-0.2	+0.030	-0.263	+0.850	+0.408	-0.184	+0.860	+0.447	-0.424	KBLa	4
	, <b>-</b> 0+	+0.327	-0.964	+0.807	+0.326	+0.151	+1.008	+0.563	-0.720	KaLa	
6		4	-0101	10 010			12 21A	10 11	888 E-	R ~ R R	
34	-1.7	-0.692	-2.458	-1.215	-0.360	+0.055	-1.211	-0.164	-3.964	Total	
38	-1.6	-0.536	-0.333	-1.238	-0.411	+0.127	-1.208	-0.386	-0.231	KB La	m
80	-1.6,	-0.536	-0.333	-1.238	-0.411	+0.127	01.208	-0.386	-0.231	KaLa	
4	, c 0						DU DI	500 CT	-5 101	K~ KB	
~	์ ม	n 1	н 1 1	n = 2	n = 1	n = -1	n = 2	n = 1	l- = u		
<u>.</u>	.nrn >	ge in < 1	\$ chan	r1 >	ge in <	s chan	r <sup>n</sup> 12 >	ige in <	s chan	SHELL	7
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Figure 2.2.1 The HF function  $f(r_{12})$  for the  $(1s^22p)^2P$  state for Li, Be<sup>+</sup>, B<sup>2+</sup>, C<sup>3+</sup>, N<sup>4+</sup> and O<sup>5+</sup> plotted against the scaled distance  $2r_{12}$  (in atomic units). (A) The KaKβ-shells, (B) the KaLa-shells, (C) the KβLa-shells, and (D) the total distribution when normalized to unity.





Figure 2.2.2 The Coulomb holes  $\Delta f(r_{12})$  vs  $2r_{12}$  for the  $(1s^22p)^2P$  state derived for Li, Be<sup>+</sup>, B<sup>2+</sup>, N<sup>4+</sup> and O<sup>5+</sup>. (A) The KaL\beta-shells, (B) the KaLa-shells, (C) the K $\beta$ La-shells and (D) the total Coulomb hole for each Z obtained here by

## taking $1/3 \sum_{\substack{i < j}}^{3} \Delta f_{ij}(r_{12})$ .

For the intrashells, the curves are ordered from right to left as Z increases.

For the inter-shells and the total system, the curves are ordered by noting that, at  $2r_{12}=12$ ,  $\Delta f(r_{12})$  decreases in value as Z increses.



and KpL<sub> $\alpha$ </sub> (-----) shells in the  $(1s^2 2p)^2 p$  state of (A) Li, (B) Be<sup>+</sup> and (C) N<sup>4+</sup>. The Sum Total (-----) of these contributions is given by KaKB + KaLa + K $\beta$ La. The  $\Delta f(r_{12})$ -scale for Sum Total Coulomb hole is the same as that for the  $K\alpha K\beta$ -shell which is shown on the diagram. All  $\Delta f(r_{12})$  scales are marked in increments of 2 x Q, where Q is A comparison of the Coulomb holes vs.  $2r_{12}$  for the KaK $\beta$ (----), KaLa(----given at the top of each ordinate. each Figure 2.2.3 left of the

Figure 2.2.4

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(see over)

Figu	<b>re 2.</b> 2	<b>F</b>	he HF	surf	A Ce	J(E 12'	r, ( <sub>1</sub> r	. (r	2, r 1)	for	the
Li,	Be <sup>+</sup>	and	+ + Z	r u	the	(18 <sup>2</sup> 2	2p) <sup>2</sup> p	state		(Y)	The
Κα Κβ	-shells	(top	IOW),	(B)	the	Kala-	shells	(mid	dle rc	, ( MC	(c)
the	Kß La - s	hells	(bot)	to	row)		Note	that	each	col	umn
COLL	esponds	to a	given	atoi							

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Figure 2.2.5

(see over)

**Figure 2.2.5** The partial Coulomb hole  $\Delta g(r_{12}, r_1)$  vs.  $(r_{12},r_1)$  for the Li, Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^22p)^2p$  state. (A) The  $K\alpha K\beta$ -shells (top row), (B) the KaLa-shells (middle row) and (C) the K $\beta$ L $\alpha$ -shells (bottom row). Note that each column

corresponds to a given atom.







Figure 2.2.6 (see over)

for Li,  $Be^+$  and  $N^{4+}$  in the  $(1s^22p)^2p$  state. Surfaces are shown for  $\theta_1 = 0.30^{\circ}$ , 60° and 90°, where  $\theta_1$  is measured relative to the symmetry axis of the positive lobe of the 2p **Figure 2.2.6** The Hf surface  $g(r_{12}, r_{1}, \theta_{1})$  for the KaLa-shell orbital. Note that each row corresponds to a given atom with each surface having scales identical with that for  $\theta_1 = 0^{\circ}$ .



Figure 2.2.7

(see over)

Figure 2.2.7 The HF surface  $g(r_{12}, r_{1}, \theta_{1})$  for the KBL $\alpha$ -shell for Li,  $Be^+$  and  $N^{4+}$  in the  $(1s^22p)^2p$  state. Surfaces are relative to the symmetry axis of the positive lobe of the 2p shown for  $\theta_1 = 0^{\circ}$ , 30°, 60° and 90°, where  $\theta_1$  is measured orbital. Note that each row corresponds to a given atom with each surface having scales identical with that for  $\theta_1 = 0^{\circ}$ . ,


Figure 2.2.8 (see over)

**Figure 2.2.8** The partial Coulomb hole  $\Delta g(r_{12}, r_1, \theta_1)$  for the  $K\alpha L\alpha$ -shell for Li, Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^2 2p)^2 P$  state. The  $\Delta g(r_{12}, r_1, \theta_1)$  surfaces are shown for  $\theta_1 = 0^{\circ}$ , 30°, 60° and the positive lobe of the 2p orbital. Note that each row 90°, where 0<sub>1</sub> is measured relative to the symmetry axis of corresponds to a given atom with surface having scales identical with that for  $B_1 = 0^{\circ}$ .



Figure 2.2.9

(see over)

Figure 2.2.9 The partial Coulomb hole  $\Delta g (r_{12}, r_1, \theta_1)$  for and  $90^{\circ}$ , where  $\theta_{1}$  is measured relative to the symmetry axis the KBL $\alpha$ -shell for Li, Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^22p)^2p$  state. of the positive lobe of the 2p orbital. Note that each row The  $\Delta g(r_{12}, r_{1}, \theta_{1})$  surfaces are shown for  $\theta_{1} = 0^{\circ}, 30^{\circ}, 60^{\circ}$ corresponds to a given atom with surface having scales identical with that for  $\theta_1 = 0^{\circ}$ .



Figure 2.2.10

(see over)

densities  $D(r_1, r_2)$  for Li, Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^2 2p)^2 P$ (middle row), and (C) the KBLa-shells (bottom row). Note Figure 2.2.10 A comparison of the HF two-partical radial state. (A) the  $K\alpha K\beta$ -shells (top row), (B) the  $K\alpha L\alpha$ -shells that each column corresponds to a given atom.







Figure 2.2.11 (see over) .

Li, Be<sup>+</sup> and N<sup>4+</sup>. (A) The KuKB-shells (top row), (B) the relative to the HF distribution, for the  $(1s^22p)^2p$  state for **Figure 2.2.11 A** comparison of the change in  $D(r_1, r_2)$ , Kala-shells (middle row) and (C) the KBLa-shells (bottom row). Note that each column corresponds to a given atom.









## PART THREE

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ELECTRON CORRELATION IN LI-LIKE IONS IN MOMENTUM SPACE

3.1  $(1s^22s)^2$ S- AND  $(1s^22p)^2$ P-STATES

## CHAPTER 3.1.1

#### INTRODUCTION

The effects of correlation in the ground  $(1s^22s)^2S$  state and excited  $(1s^22p)^2p$  state of Li-like ions have been examined so far in position space. The analysis was executed, using the 45 configuration wavefunction of Weiss<sup>(25)</sup>, by determining Coulomb holes<sup>(63)</sup> and various expectation values for each electronic shell. The expectation values were used to calculate several statistical correlation coefficients  $\tau$  and the percentage change in the expectation values  $\langle r_{12}^n \rangle$ ,  $\langle r_1^n r_2^n \rangle$  and  $\langle r_1^n \rangle$ which arises due to correlation. The description of an individual electronic shell, at both the HF and the correlated level, was obtained by partitioning the second-order density for the total atom into its pair-wise components. Variations in the importance of correlation throughout different regions of position space were studied by means of  $\Delta g(r_{12}, r_1)$  for both the ground and excited states of the three-electron systems. Global assessments of the angular and radial components of electron correlation for the  $K\alpha K\beta$ -shell were obtained in terms of  $\Delta \tau$  - the change in a particular  $\tau$  value when measured relative to its HF result. In the light of the results obtained in position space, a parallel investigation of the Li-like ions will now be carried out in momentum space.

In recent years, considerable progress has been made in the experimental and theoretical determination of electron distributions in momentum space. The knowledge of electron

momentum distributions in atoms and molecules should give information about electron-nuclear and electron-electron interactions. This is due to the fact that the momentum of an electron is the result of the forces exerted upon it by the nuclei and other electrons. There exist two fundamentally different approaches to the calculation of momentum space wavefunctions. In the first method the Schrodinger equation is transformed from a differential equation in position space to an integral equation in momentum space. In fact, this method of evaluation of the momentum space wavefunction has met with very little general success. The method has been used, however, by McWeeny and Coulson<sup>(79)</sup> for the helium atom and the hydrogen molecule. Fortunately, the second method seems to be a more attractive approach; this method involves converting the position space wavefunction into the momentum space representation by using the Dirac transformation<sup>(80)</sup> procedure.

From the study of  $He^{(81)}$  in both position and momentum space, it was found that in momentum space the effects of radial and angular correlation work in opposition, whereas, by contrast, these components are known to work in unison in position space. Consequently, momentum space is useful in order to examine the correlation problem, in particular the differences between the radial and angular properties of correlation for both atoms and molecules. Furthermore, the momentum transformation gives greater emphasis to the outer regions of the wavefunction than in position space and is therefore especially useful when considering the behaviour of the valence electrons within a system. By comparison

with position space, it has been found that in a study of some two-electron systems (71,83), such differences in behaviour of angular and radial correlation effects give rise to a relatively complicated structure for the momentum space Coulomb hole and the partial holes; thus, for momentum space, it is preferable to use the term 'shift' rather than 'hole'<sup>(82)</sup>. Mobbs and Banyard<sup>(83)</sup> have used the partitioning technique of Sinanoglu to study momentum space correlation effects in the ground state of the Be atom. More recently Youngman<sup>(84)</sup> has used the same method to study Coulomb shifts and a variety of other correlation properties in the <sup>2</sup>S- and <sup>2</sup>P-states of the neutral Li atom. In the following chapters, Youngman's analysis in momentum space is extended to a sequence of Li-like ions in both  $^{2}$ S- and  $^{2}$ Pstates, thus enabling comparisons to be made with our previous work in position space. In the examination of the Z-dependent trends for such correlation effects it is convenient to include here the relevent results obtained by Youngman for the neutral Li atom in momentum space.

For both ground and excited states of the three-electron ions, the Coulomb shift, partial Coulomb shift, expectation values and other properties in momentum space are derived from the Weiss<sup>(25)</sup> 45 configuration wavefunctions. The HF reference states for the systems considered are taken, as before, from the work of Weiss<sup>(25)</sup>. For the <sup>2</sup>P state, modifications in the evaluation of Coulomb shifts and partial Coulomb shifts are necessary. The  $\theta_1$  - dependent partial shift  $\Delta g(p_{12}, p_1, \theta_1)$ , where the angle  $\theta_1$  is measured relative to the symmetry axis of the system, is also of

interest for the inter-shells. The present investigation, together with the earlier position space study will provide an overall view of correlation effects within the individual shells for this series of three-electron ions.

Atomic units are employed throughout this work.

# CHAPTER 3.1.2

### CALCULATIONS AND RESULTS

Following Youngman<sup>(84)</sup>, the analysis of electron momentum distributions in the Li-like ions is performed here using the 45-term CI correlated wavefunctions of Weiss<sup>(25)</sup> for the ground and excited states. The HF reference wavefunction is also taken from the work of Weiss<sup>(26)</sup>.

As in our earlier analysis in position space, the normalized HF wavefunction for each atomic state examined here was written in the form of a single determinant (see Appendix A.1). Using the procedure of Sinanoglu, the correlated wavefunction may be written as

$$\Psi_{corr}(1,2,...,N) = c[A\{\Pi(1,2,...,N)(1+\sum_{i=1}^{N} f_i/*]$$

$$+1/J(2!)\sum_{i < j}^{N} U_{ij}/*_{i}*_{j} + 1/J(3!)\sum_{i < j < k}^{N} U_{ijk}/*_{i}*_{j}*_{k} + ... \} 3.1.1$$

where the labels i,j and k refer to members of the basis set of occupied HF spin-orbitals  $\{*\}$  and  $\Pi(1,2,\ldots,N)$  is the product of all such normalized functions. The function  $f_i$ is an orbital correction term and  $U_{ij}$  is the paircorrelation function associated with  $*_i$  and  $*_j$ . The remaining notation and the orthogonality conditions imposed on  $f_i$ ,  $U_{ij}$ , etc have been given earlier in this work.

As before, electron correlation can be investigated by examining the differences between the correlated twoparticle density  $\Gamma_{corr}(\underline{x}_1,\underline{x}_2)$  and the corresponding HF

density  $\Gamma_{\rm HF}(\underline{x}_1,\underline{x}_2)$ . In this instance,  $\underline{x}_1$  represents the combined momentum space and spin co-ordinates of electron 1. The definition of  $\Gamma(\underline{x}_1,\underline{x}_2)$  in terms of an N-particle wavefunction again follows that of McWeeny and Sutcliffe<sup>(67)</sup>. The two-particle densities  $\Gamma(\underline{x}_1,\underline{x}_2)$  for the HF and correlated wavefunctions can be partitioned into their pairwise components (i,j) by writing, as previously (see equations (2.1.41) and (2.1.43)),

$$\Gamma_{\rm HF}(\underline{x}_{1},\underline{x}_{2}) = 1/2 \sum_{\substack{i < j \\ i < j}}^{N=3} \{ \phi_{\underline{i}}(\underline{x}_{1}) \phi_{\underline{j}}(\underline{x}_{2}) - \phi_{\underline{j}}(\underline{x}_{1}) \phi_{\underline{i}}(\underline{x}_{2}) \}^{2}, 3.1.3$$

$$\Gamma_{corr}(\underline{x}_{1}, \underline{x}_{2}) = \sum_{\substack{i < j \\ i < j}}^{N=3} \{ \phi_{\underline{i}}(\underline{x}_{1}) \phi_{\underline{j}}(\underline{x}_{2}) - \phi_{\underline{j}}(\underline{x}_{1}) \phi_{\underline{i}}(\underline{x}_{2}) \} [$$

$$\langle \Psi_{corr} | \pi_{\underline{i}} \rangle / \langle \Psi_{corr} | \pi \rangle - 1/2 \{ \phi_{\underline{i}}(\underline{x}_{1}) \phi_{\underline{j}}(\underline{x}_{2}) - \phi_{\underline{j}}(\underline{x}_{1}) \phi_{\underline{j}}(\underline{x}_{2}) \} ] \qquad 3.1.4$$

The integrations in  $\langle \Psi_{corr} | \Pi_{ij} \rangle$  are over all the co-ordinates occurring in  $\Pi_{ij}$  and thus we obtain a function of  $\underline{x}_1$  and  $\underline{x}_2$  only (see Appendix A.1).

The HF and the correlated wavefunctions for the  ${}^{2}S$  and  ${}^{2}P$  states of the Li-like ions, are formed in position space from Slater type orbitals (STO's). To obtain the corresponding wavefunctions in momentum space, the general expression for the Slater type orbital is converted  ${}^{(80)}$  into momentum space by applying the usual Dirac procedure described in Appendix A.3, to give

$$N/(2/\pi)(1!)i^{1-2n}(2p)^{1}\frac{\partial^{n-1}}{\partial \xi^{n-1}}[(\xi^{2}+p^{2})^{-(1+1)}]Y_{1m}$$
, 3.1.5

where  $\xi$  is the appropriate orbital exponent, n is the principal quantum number and 1 is the azimuthal quantum number. The function  $Y_{lm}$  is a normalized spherical harmonic in the Dirac phase convention.

By analogy with the work of Coulson and Neilson<sup>(63)</sup> in position space, Banyard and Reed<sup>(82)</sup> obtained the 'Coulomb shift' in momentum space from the definition

$$\Delta f(p_{12}) = f_{corr}(p_{12}) - f_{HF}(p_{12}) , \qquad 3.1.6$$

where  $f(p_{12})$  associated with the pair (i,j) is given by

$$f_{ij}(p_{12}) = \int \Gamma_{ij}(p_1, p_2) dp_1 dp_2 / dp_{12} \qquad 3.1.7$$

The limits of integration are analogous to those discussed by Coulson and Neilson<sup>(63)</sup> in position space and it is to be noted that spin has been integrated out of equation (3.1.7). The details concerning the calculation of  $f(p_{12})$  are dicussed in Appendix A.2. The Coulomb shift  $\Delta f(p_{12})$  is the change, due to correlation, in the distribution function  $f(p_{12})$  for a given magnitude of the momentum difference  $p_{12} = |p_1 - p_2|$  between electrons 1 and 2. Each  $f(p_{12})$  is normalized to unity.

The  $f_{\rm HF}(p_{12})$  distribution and the Coulomb shifts  $\Delta f(p_{12})$ vs.  $z^{-1}p_{12}$  for the KaK $\beta$ -, KaLa-, and K $\beta$ La-shells of the Lilike ions in the <sup>2</sup>S state are shown in Figures 3.1.1-2. For the <sup>2</sup>P state, the Coulomb shift calculations are more complicated than the <sup>2</sup>S state due to the non-zero angular

momentum (see Appendix A.2), the corresponding results for  ${}^{2}P$  are shown in Figures 3.1.11-12. In addition, the above Figures contain the total normalized distribution for  $f_{\rm HF}(p_{12})$  and  $\Delta f(p_{12})$ ; the normalized total is given by (K $\alpha$ K $\beta$  + K $\alpha$ L $\alpha$  + K $\beta$ L $\alpha$ )/3. The curves for the individual shells are compared with their sum total holes (where the sum total is given by the sum of the electronic shell results only) for Li, Be<sup>+</sup> and N<sup>4+</sup> in Figure 3.1.4 for <sup>2</sup>S state, and Figure 3.1.14 contains the <sup>2</sup>P results. In addition to the above we have obtained insight into the shape of the f(p<sub>12</sub>) for both HF and correlated wavefunctions by evaluating the expectation values

$$\langle p_{12}^n \rangle = \int f(p_{12}) p_{12}^n dp_{12}$$
 3.1.8

for n=-1, 1 and 2. Clearly, different regions of the  $f(p_{12})$ curve will be emphasised by the function  $p_{12}^n$  for each value of n. A particularly useful concept for displaying the spread of the momentum density is the standard deviation  $\Delta(p_{12})$ , which is defined by

$$\Delta(p_{12}) = \int [\langle p_{12}^2 \rangle - \langle p_{12} \rangle^2] \qquad 3.1.9$$

The results of  $\langle p_{12}^n \rangle$  and  $\Delta(p_{12})$  are presented in Table 3.1.1 and Table 3.1.6 for the <sup>2</sup>S and <sup>2</sup>P states, respectively.

The definition of the  $g_{HF}(p_{12},p_1)$  function and the partial Coulomb shift  $\Delta g(p_{12},p_1)$  in momentum space follow those for the corresponding position space quantities.  $\Delta g(p_{12},p_1)$  measures the influence of correlation when a test

+

electron 1, has a momentum of a given magnitude p<sub>1</sub>. For each electronic shell, the partial Coulomb shift is defined such that

$$\int \Delta g(p_{12}, p_1) dp_1 = \int g_{corr}(p_{12}, p_1) dp_1 - \int g_{HF}(p_{12}, p_1) dp_1$$
  
=  $\Delta f(p_{12})$  . 3.1.10

The  $g_{HF}$  and  $\Delta g$ -results for each shell are displayed for Li, Be<sup>+</sup>and N<sup>4+</sup> as surfaces in Figures 3.1.5-6 for the <sup>2</sup>S state and Figures 3.1.15-16 for <sup>2</sup>P state. For the <sup>2</sup>P state, we can also define the functions  $g(p_{12}, p_1, \theta_1)$  and  $\Delta g(p_{12}, p_1, \theta_1)$ where  $\theta_1$  is measured relative to the symmetry axis of the system. These functions are defined such that

$$\int_{0}^{\infty} g(p_{12}, p_{1}, \theta_{1}) \sin \theta_{1} d\theta_{1} dp_{1} = \int_{0}^{\infty} g(p_{12}, p_{1}) dp_{1} = f(p_{12}) \cdot 3.1.11$$

The  $\theta_1$ -dependent functions for the Li, Be<sup>+</sup> and N<sup>4+</sup> intershells are shown in Figures 3.1.17-20.

As in position space, the angular effect of correlation can be investigated by calculating the expectation values  $\langle \underline{p}_1, \underline{p}_2/p_1^n \underline{p}_2^n \rangle$  for n = 0, 1 and 2. These expectation values involve the angle  $\gamma$  between the momentum vectors  $\underline{p}_1$  and  $\underline{p}_2$ of electrons 1 and 2, and therefore they are sensitive to angular correlation. It is to be noted that the calculation of these expectation quantities requires the evaluation of a product of three spherical harmonics<sup>(85)</sup>. The results for these angular properties are shown in Table 3.1.1 and Table 3.1.6 for the <sup>2</sup>S and <sup>2</sup>P states, respectively.

To gain some understanding of the effects of correlation on radial properties in momentum space, we calculated the electron pair radial density  $D(p_1, p_2)$  for Li, Be<sup>+</sup> and N<sup>4+</sup> in each electronic shell using both the HF and correlated wavefunctions. Radial correlation effects are illustrated by calculating the changes in the two-particle radial momentum distribution  $D(p_1,p_2)$  relative to the HF value. Figures 3.1.7-8 illustrate  $D_{HF}(p_1, p_2)$  and  $\Delta D(p_1, p_2)$  for each shell for selected ions in the <sup>2</sup>S state. Figures 3.1.21-22 show the  $D_{HF}(p_1,p_2)$  and  $\Delta D(p_1,p_2)$  surfaces for the same ions in the KaK $\beta$ -, KaLa- and K $\beta$ La-shells of the <sup>2</sup>P-state. To complete the radial properties we evaluated the one- and two-particle radial expectation values  $\langle p_1^n \rangle$  and  $\langle p_1^n p_2^n \rangle$ . The results are reported in Tables 3.1.2-3 and Tables 3.1.7-8 for <sup>2</sup>S and <sup>2</sup>P states, respectively. For the purposes of discussion, the one-particle radial density distributions  $D(p_1)$  derived from the HF wavefunctions are presented in Figures 3.1.9 and 3.1.23 for the <sup>2</sup>S and <sup>2</sup>P states in the  $K\alpha K\beta$ -,  $K\alpha L\alpha$ - and  $K\beta L\alpha$ -shells for Li, Be<sup>+</sup> and N<sup>4+</sup>.

The radial and angular components of electron correlation may be assessed in a global manner by calculating various statistical correlation coefficients. Following the position space analysis, the radial and angular coefficients take the forms

$$\tau_{radial} = (\langle p_1^n p_2^n \rangle - \langle p_1^n \rangle^2) / (\langle p_1^{2n} \rangle - \langle p_1^n \rangle^2) \qquad 3.1.12$$

$$\tau_{angular} = \langle (\underline{p}_1/p_1^{1-n}), (\underline{p}_2/p_2^{1-n}) \rangle / \langle p_1^{2n} \rangle$$
 3.1.13

where  $\tau_{radial}$  gives  $\tau_p$  and  $\tau_{1/p}$  when n=1 and -1, respectively. These quantities give emphasis, in turn, to large and small values of the magnitude of p. For the angular coefficients, n=1, -1 and 0 correspond to  $\tau_{\gamma}$ ,  $\tau_{\gamma}$ , and  $\tau_{\chi\mu}$ , respectively, where, as defined earlier,  $\gamma$  is the angle between the electronic momentum vectors  $\underline{p}_1$  and  $\underline{p}_2$ . Table 3.1.4 contains the  $\Delta \tau$  results for <sup>2</sup>S state for each shell for the Li-like ions, where  $\Delta \tau = \tau_{corr} - \tau_{HF}$ : Table 3.1.9 contains the  $^2P$  results. All the  $\tau$  for the HF wavefunction are zero except for KaLa-shell in the <sup>2</sup>P state. These  $\tau$  values are presented in Table 3.1.10. The correlation changes in  $\tau$  have been plotted against  $2^{-1}$  in Figures 3.1.10 and 3.1.24 for the  $K\alpha K\beta$ -shell in both states. Table 3.1.4 also contains the percentage change of each  $f_{\mu\nu}(p_{12})$  probability density. The normalized total for Y, was determined from the normalized Coulomb shifts shown in Figure 3.1.2D. In this instance, Y is equal to the area of the curve below or above the p<sub>12</sub> axis multiplied by 100%. Finally, in Tables 3.1.5 and 3.1.11 we present the percentage changes, due to correlation, in  $\langle p_{12}^n \rangle$ ,  $\langle p_1^n \rangle$  and  $\langle p_1^n p_2^n \rangle$  for n=-1, 1 and 2 for the <sup>2</sup>S and <sup>2</sup>P states, respectively. Notice that the normalized total used in each Table is given by  $(K\alpha K\beta + K\alpha L\alpha + K\beta L\alpha)/3$ .

# CHAPTER 3.1.3 DISCUSSION OF THE (1s<sup>2</sup>2s)<sup>2</sup>s state

The KaKB-shell

Figure 3.1.1(A) shows the  $Z^{-1}$  scaled plots of the HF interparticle densities in the KaLB-shell. It is to be noted that as Z increases not only does  $f_{HF}(p_{12})$  become more diffuse but also decreases in magnitude. Comparing these curves with those in position sapce, see Figure 2.1.1(A), we observe the fundamental change due to the different spaces. The interparticle distribution function in position space show that as Z increases  $f_{HF}(r_{12})$  becomes less diffuse and increases in magnitude. This behaviour is supported by inspection of the corresponding expectation values  $\langle p_{12}^n \rangle$ (see Table 3.1.1) and  $\langle r_{12}^n \rangle$  (see Table 2.1.3), when n=-1, 1 and 2. From these expectation values we see that for the KaKB-shell the momentum results are greater than the position results when n is positive and vice-versa when n is The Coulomb holes in position space can be negative. brought into reasonable coincidence by scaling the r<sub>12</sub> axis Zr<sub>12</sub>, where Z is the nuclear charge (see Figure as 2.1.2(A)). In momentum space, the  $\Delta f(p_{12})$  curves suggest an inverse scaling with respect to Z and the scaled Coulomb shifts are shown in Figure 3.1.2(A) for Li,  $Be^+$ ,  $B^{2+}$ ,  $N^{4+}$ and 0<sup>5+</sup>. These curves reveal the correlation effects relative to the f<sub>HF</sub>(p<sub>12</sub>) properties. We see from the  $\Delta f(p_{12})$  curves that the zeros of the scaled curves are in very good agreement. The curves for Z > 4 cross the axis in

the region  $Z^{-1}p_{12} = 1.5$ , whereas the curve for Z = 3 crosses the axis twice: firstly in the region  $Z^{-1}p_{12} \approx 0.35$  and then again when  $Z^{-1}p_{12} = 1.5$ . The behaviour of the Coulomb shift in  $Z^{-1}p_{12} > 0.35$  is seen to be well-ordered with respect to Z, whereas the curves are not so well-ordered when  $Z^{-1}p_{12} \leq$ 0.35, for example the Li Coulomb shift has negative values in this region.

In Figure 3.1.3 we show a comparison of the Coulomb shifts for the KaK<sub>β</sub>-shells in Be<sup>(83)</sup>, Be<sup>+</sup> and Be<sup>2+(77)</sup>; also included are the  $\Delta f(p_{12})$  curves for  $K \alpha K \beta$  in Li<sup>+(82)</sup> and Li. For Z = 4, we observe that although the Be<sup>+</sup>, Be<sup>2+</sup> and Be functions give results which are the same when  $2^{-1}p_{12} > 1.5$ , significant differences exist for  $0 < 2^{-1} p_{12} < 1.5$ . For two-electron systems, Banyard and Reed<sup>(82)</sup> established that, at small p<sub>12</sub>, the radial component of electron correlation gives rise to negative values for  $\Delta f(p_{12})$  whereas, by contrast, angular correlation produces a curve which is initially positive. From the K-shell in Be<sup>+</sup> and Be, it appears that the occupation of the L shell by one- and twoelectrons, respectively, causes an initial cancellation between the angular and radial components. In general, we conclude that for a given 2 the  $\Delta f(p_{12})$  curve for the Kshell increases at small p<sub>12</sub> when an electron is added to the L-shell. These differences between  $Be^+$ ,  $Be^{2+}$  and Be at small p<sub>12</sub> are in general accord with a comparison between the corresponding  $\Delta \tau$  values. It was found that the  $\Delta \tau_{1/p}$ values are ordered in magnitude as Be << Be<sup>+</sup> << Be<sup>2+</sup> i.e. the  $\Delta \tau_{1/p}$  values are -0.0058, -0.0095 and -0.0197 for  $Be(K_{\alpha}K_{\beta})$ ,  $Be^+(K_{\alpha}K_{\beta})$  and  $Be^{2+}$ , respectively. Therefore, by

comparison with  $Be^{2+}$ , radial correlation at small momenta in the  $Be^{\pm}$  and Be K-shell is inhibited by the presence of the one and two L-shell electrons. In the light of the momentum analysis by Banyard and Reed<sup>(82)</sup>, the overall behaviour of the curves in Figure 3.1.2(A) suggests that angular correlation has, on balance, the major influence in the Kshell of Li-like ions. The comparison of the  $\Delta f(p_{12})$  curves in the K $\alpha$ K $\beta$ -shell with respect to Z can be shown by inspection of the percentage change of the momentum density  $\gamma$ %.

Let us now examine the interparticle density  $f_{HF}(p_{12})$ and the Coulomb shift  $\Delta f(p_{12})$  for the KaK<sub>β</sub>-shell as a function of the momentum of electron 1, that is  $g_{HF}(p_{12}, p_1)$ and  $\Delta g(p_{12}, p_1)$ , respectively. The  $g_{HF}(p_{12}, p_1)$  function and the partial Coulomb shift  $\Delta g(p_{12}, p_1)$  for Li, Be<sup>+</sup> and N<sup>4+</sup> are presented in Figures 3.1.5(A) - 6(A). The  $g_{HF}(p_{12}, p_1)$ surfaces for Li,  $Be^+$  and  $N^{4+}$  show that the maximum for each density is always located off the diagonal such that  $p_{12}$ ,  $p_1$ . The examination of the  $\Delta g(p_{12}, p_1)$  surfaces for the selected ions can be separated into three regions, depending on the value of  $p_1$ . At very small  $p_1$  there is some evidence of a small angular effect. From the  $\Delta g$ -surface a small positive maximum can be seen at small  $p_1$  and  $p_{12}$ , this feature is very easily observed in  $N^{4+}$  by comparison with Li and Be<sup>+</sup> surfaces. The cause of this positive  $\Delta g$  at small  $p_1$  and  $p_{12}$ is perhaps due to the effect of integrating out the L-shell electron when partitioning the two-particle density. Therefore, this feature should not appear in the <sup>2</sup>P state because of the orthogonality condition between the s and p

orbitals. However, when the test electron is at small  $p_1$ , the  $\Delta g(p_{12}, p_1)$  results are a mixture of radial and angular correlation with the angular component being just dominant in the small p<sub>12</sub> regions. As p<sub>1</sub> increases, i.e. when the test electron lies between the K- and L-shell regions, then the partial Coulomb shift shows a reduction and then an increase as  $p_{12}$  becomes larger. Consider the  $\Delta g$ - behaviour when p<sub>1</sub> increases further so that the electron approaches the maximum in the  $D_{HF}(p_1)$  vs.  $p_1$  graph for the K-shell. We see that the angular correlation component shows a large dominant effect for all  $p_{12}$  for all increasing  $p_1$ . This is reasonable since, if the test electron has large  $p_1$  it will be located near to the nucleus and, therefore, it will be influenced by a large, rapidly varying radial potential field. Consequently, any radial correlation effect would change the energy markedly, however, the electrons can avoid one another, without a great change in the nuclear-electron energy, by using angular correlation effects. The  $K\alpha K\beta$ - $\Delta g(p_{12}, p_1)$  diagram in Figures (3.1.6(A) reveals the behaviour of the charateristics mentioned above.

As Z increases, the  $g_{HF}$  and  $\Delta g$ -characteristics (but not their location and magnitude) are unchanged, and the whole pattern expands, as expected, to fill larger  $p_{12}$  and  $p_1$ values. As in position space for the K $\alpha$ K $\beta$ -shell, there appears to be no immediately obvious connection between the relative positioning of the maximum in the  $g_{HF}(p_{12}, p_1)$ surfaces and the maxima and minima in the corresponding  $\Delta g(p_{12}, p_1)$  diagram. As Z increases, the  $g_{HF}(p_{12}, p_1)$  and  $\Delta g(p_{12}, p_1)$  surfaces spread over greater  $p_1$  and  $p_{12}$  ranges

and consequently, the maxima and minima decrease in magnitude. Comparing the heights of the maxima on the diagonal with those of the parallel feature of  $\Delta g(p_{12}, p_1)$ shows that, as Z increases, the ratio is 1.88, 2.32 and 2.87 for Z = 3, 4 and 7, respectively. Such an increase implies that the angular effect at large  $p_1$  becomes relatively more important than the radial effect at small  $p_1$ . All these observations are consistent with views about angular and radial correlation for the KaK $\beta$ -shell in position space, as the density tightens around an increasing nuclear charge.

Figures 3.1.7(A) and 3.1.8(A) show the  $D_{HF}(p_1, p_2)$  and  $\Delta D(p_1, p_2)$  surfaces for the KaK<sub>β</sub>-shell in Li, Be<sup>+</sup> and N<sup>4+</sup>. Although these surfaces possess a strong resemblance to their counterparts in position space,  $D_{HF}(p_1, p_2)$  and  $\Delta D(p_1, p_2)$  reveal obvious differences with respect to variations in Z. As Z increases not only does  $\Delta D(p_1, p_2)$ become more diffuse but it also decreases in magnitude, whereas, in position space, the converse occurs. The behaviour of  $\Delta D(p_1, p_2)$  is also reflected in the related expectation values  $\langle p_1^n p_2^n \rangle$ . Radial correlation causes a decrease in  $\langle p_1^n p_2^n \rangle$  for n = -1, 1 and 2, which is also shown by the percentage change of  $\langle p_1^n p_2^n \rangle$  due to the correlation Tables 3.1.2 - 3 contains a comparison of the HF effect. and correlated one- and two-particle expectation values for the  $K\alpha K\beta$ -shell of the Li-like ions. The one-particle radial momentum density  $D(p_1)$  may be obtained by integrating  $D(p_1, p_2)$  with repect to  $p_2$ . For the KaK<sub>β</sub>-shell, the  $D_{HF}(p_1)$ curves for Li,  $Be^+$  and  $N^{4+}$  are shown in Figure 3.1.9.

An overall assessment of angular and radial correlation components in different regions of momentum space for the Kshell is provided by the change in the correlation coefficients listed in Table 3.1.4. Figure 3.1.10 shows that the changes in the radial correlation coefficient  $\tau$ possess a negative sign, whereas changes in the angular correlation coefficient  $\tau$  have a positive sign for all Z; by contrast, in position space, both components possessed negative signs for each Z.

## The KaLa- and KBLa-Shells

Figures 3.1.1(B - C) and 3.1.2(B - C) illustrate the interparticle momentum function  $f_{HF}(p_{12})$  and the Coulomb shift  $\Delta f(p_{12})$  for the KaLa- and K $\beta$ La-shells, plotted against  $z^{-1}p_{12}$ . Examining  $f_{HF}(p_{12})$  vs.  $z^{-1}p_{12}$  for the KaLa-shell we see that it is higher valued at small p<sub>12</sub> and lower at higher  $P_{12}$  than its KaK $\beta$  counterpart. This is reasonable since the inter-shell will contain more low momentum contributions as a consequence of the L-shell occupation. Since both the KaLa and KaLß sets of curves are normalized to the same value, a reduction at large  $2^{-1}p_{12}$  for KaLa, compared with KaKB, must result in an increase in the curve at smaller  $2^{-1}p_{12}$  values as seen. The KaLa- and K $\beta$ La-curves for f<sub>HF</sub>(p<sub>12</sub>) show 2-dependent trends similar to those in the  $K_{\alpha}K_{\beta}$ - shell. From Figure 3.1.1(B - C), the  $f_{HF}(p_{12})$  curves for the KaLa-shell tend to have a flat region at small  $p_{12}$ due to the Fermi effect. As 2 increases, the  $f(p_{12})$  maxima and their locations tend to increase as we progress from a given KBLa curve to the corresponding KaLa curve.

Let us consider the Coulomb shift for both the KaLa- and KBLa-shells for Li, Be<sup>+</sup>, B<sup>2+</sup>, N<sup>4+</sup> and  $0^{5+}$ . As in position space, the Coulomb shifts for the  $K\beta L\alpha$ -shell seems greater in magnitude than those in KaLa. Furthermore, these intershell Coulomb shifts are found to be of similar shape except in the region of small  $p_{12}$ . In the KaLa-curves there is a flat region due to the Fermi effect whereas this does not occur for KBLa curves. Both sets of inter-shell Coulomb shifts tend to decrease and increase at  $2^{-1}p_{12}$  equal to 0.5 and 1.0, respectively as Z increases. Figure 3.1.2(D) (see also Figure 3.1.4) shows the normalized total Coulomb shift for each Z. These curves, which are defined by  $(K\alpha K\beta + K\alpha L\alpha)$ +  $K\beta L\alpha$ )/3, reflect the dominant effects of the KaK $\beta$  Coulomb shifts and the sum total Coulomb shifts for Li,  $Be^+$  and  $N^{4+}$ . Further comparisons are obtained by inspection of the percentage change Y% in Table 3.1.4.

Consider  $g_{HF}(P_{12},P_1)$  and  $\Delta g$  for Z = 3, 4 and 7 for both the KaLa- and K $\beta$ La-shells. These functions of  $P_{12}$  and  $P_1$ are shown in Figures 3.1.5(B - C) and 3.1.6(B - C) as surfaces. As in position space, the  $g_{HF}(P_{12},P_1)$  surfaces for the inter-shells show diagonal and parallel characteristics. The spread of these features reflects the spread of the K- and L-shells densities in  $P_1$ -space. Since the HF model indicates that the average angle between the electronic momentum vectors is 90°, then the location of the most probable distribution of the  $g_{HF}(P_{12},P_1)$  density can be estimated by using Pythagorous's theorem. The differences between  $g_{HF}(P_{12},P_1)$  for KaLa and  $g_{HF}(P_{12},P_1)$  for K $\beta$ La can be

found at small  $p_{12}$ , for all  $p_1$  values, due to the presence of the Fermi effect in the KaLa-shell. To investigate this difference in more detail, we subtracted the  $g_{HF}(p_{12}, p_1)$  for K  $\beta$  La from the  $g_{HF}(p_{12}, p_1)$  for KaLa-shell. From this difference, we found that the introduction of the Fermi effect caused the most noticeable reduction in probability at small p<sub>1</sub> and small p<sub>12</sub>. The partial Coulomb shifts for the inter-shells are shown in Figure 3.1.6(B - C) for Li,  $Be^+$  and  $N^{4+}$ . These diagrams reveal the angular and radial correlation effects. At  $p_1 > p_K$  (i.e. close to nucleus), we see that  $\Delta g$  changes from positive to negative as  $p_{12}$ increases. This behaviour is thought to be due to the dominance of angular correlation. When the test electron p<sub>1</sub>  $p_{T,i}$  we do not see a "left-right" effect as  $p_{12}$  increases, but we do see an "up-down" effect in the surface relating to the p<sub>1</sub> variation. The above features of the partial Coulomb shift seem similar to those in the He work for the 1s2s  $^{1}$ Sand  ${}^{3}S$ -states. The comparison of  $\Delta g(p_{12}, p_{1})$  for KaLa with that for KBLa shows that the positive-negative effect for the K $\beta$ L $\alpha$  shell has moved slightly to a smaller  $p_{12}$  value compared with KaLa diagram. At small  $p_{12}$  and small  $p_1$  we see a significant negative in the  $K\beta L\alpha$  diagram which was not present in KaLa due to the presence of the Fermi effect in the KaLa- shell.

To examine the influence of correlation on the twoparticle radial momentum distribution for the intershells, we have to consider the  $D_{HF}(p_1, p_2)$  and the  $\Delta D(p_1, p_2)$ diagrams shown in Figures 3.1.7(B - C) and 3.1.8(B - C). Figures 3.1.7(B - C) reveal that the inter-shells possess an

overall similarity in their  $D_{\rm HF}(P_1,P_2)$ -surfaces, although, variations do exist. For the KaLa-shell, the principal maxima are slightly greater than those for the K $\beta$ La-shell for Li, Be<sup>+</sup> and N<sup>4+</sup>. Such a difference between these normalized distributions is a consequence of the Fermi effect giving a reduced probability for the KaLa-curve in the region of small  $P_1 \approx P_2$  when compared with the K $\beta$ La result. The  $\Delta D(P_1,P_2)$ -surfaces not only reveal correlation effects but, naturally, reflect the main features of the  $D_{\rm HF}(P_1,P_2)$ -surfaces. These changes due to correlation are in keeping with the percentage change shown in Table 3.1.5. From Table 3.1.5, the percentage change in  $\langle P_1^n P_2^n \rangle$  for KaLa is greater than the corresponding K $\beta$ La value for all Z.

The percentage of each f<sub>HF</sub>(p<sub>12</sub>) probability density which has been redistributed due to electron correlation are shown in Table 3.1.4. These values are smaller than those in position space for the Li-like ions. For the He-like ions Reed<sup>(77)</sup> found that the fraction in momentum space is about one-third of the value obtained in position space. Further comparison between the position and momentum results can also be made by inspection of the radial and angular coefficients shown in Table 2.1.8 and 3.1.4. In position space we found that for the  $K\alpha K\beta$ -shell, the radial and angular coefficients  $\Delta \tau$  are of negative sign, but by contrast, in momentum space these components show a negative sign and a positive sign, repectively. This finding holds for the whole atom in the series of the Li-like ions. The  $\Delta \tau$  results for the KaK<sub>β</sub>-shell are shown in Figure 3.1.10 and reveal that the  $\Delta \tau_{\gamma}$  (= $\Delta \cos \gamma$ ) for momentum space shows a
positive value, whereas a negative sign can be found in the corresponding quantity in position space.

# <u>CHAPTER 3.1.4</u> <u>DISCUSSION OF THE (1s<sup>2</sup>2p)</u> <sup>2</sup><u>P STATE</u>

#### The KaKB-shell

As might be expected, the interparticle densities in momentum space,  $f_{HF}(p_{12})$ , for Li, Be<sup>+</sup>, B<sup>2+</sup>, C<sup>3+</sup>, N<sup>4+</sup> and O<sup>5+</sup> behave as those for the  $K\alpha K\beta$ -shell in the <sup>2</sup>S state. Figure 3.1.11(A) reveals that the maximum of the  $f_{HF}(p_{12})$ probability distribution decreases as Z increases. This behaviour also can be supported by the inspection of the interparticle expectation value  $\langle p_{12} \rangle$  shown in Table 3.1.1. From Figure 3.1.12(A) we found that, for Li-like ions, the introduction of radial effects causes a reduction in  $\Delta f(p_{12})$ at small p<sub>12</sub>. For the three-electron systems, the ionic curves of the Coulomb shift in the excited state show a high degree of similarity with those in <sup>2</sup>S in the region when  $z^{-1}p_{12} > 0.5$ , but display differences when  $z^{-1}p_{12} \leq 0.5$ . These differences between  ${}^{2}S$  and  ${}^{2}P$  for  $\Delta f(p_{12})$  at small  $z^{-1}p_{12}$  are in general accord with a comparison between the corresponding  $\Delta \tau$  values (see Figures 3.1.10 and 3.1.24). Although the KaKB-shell angular correlation coefficients for the  $^{2}$ P state are only marginally smaller than those in  $^{2}$ S for a given Z, it is seen that the  $\Delta \tau_p$  and  $\Delta \tau_{1/p}$  values in <sup>2</sup>p are noticeably larger than those in the <sup>2</sup>S state. From the Coulomb shift  $K\alpha K\beta$ -diagram we see that the zeros of the scaled curves are in excellent agreement. These curves cross the axis twice; firstly in the region  $2^{-1}p_{12} = 0.5$  and then again when  $z^{-1}p_{12} = 1.5$ . The zeros of these shifts are

in close agreement with those of the He-like ions<sup>(82)</sup>. The  $\Delta f(p_{12})$  comparisons for the KaKβ-shell in Li(<sup>2</sup>P), Li(<sup>2</sup>S) and  $Li^+(^1S)$ , and also for  $Be^+(^2P)$ ,  $Be^+(^2S)$  and  $Be(^1S)$  are shown in Figure 3.1.13. We see that all the various Z=4 and Z=3curves cross the  $2^{-1}p_{12}$  axis at 1.5. Each set of curves then splits again into two groups, for Z=3 and 4, respectively, but each curve possesses a large maximum and large minimum in  $\Delta f(p_{12})$  at about  $z^{-1}p_{12} \approx 0.9$  and 2.1, respectively. Also we note that at  $z^{-1}p_{12} \approx 0.9$  and 2.1, the ordering of the Z=3 curves differs from the ordering of the Z=4 curves. When  $Z^{-1}p_{12} \approx 0.9$  and 2.1 we note that the  $\Delta f(p_{12})$  for  $|^2 p| > |^2 S|$ . As  $z^{-1} p_{12}$  becomes larger than 2.1, the difference between the  $^{2}P$  and  $^{2}S$  curves gets smaller as z increases. But when  $z^{-1}p_{12}$  gets smaller than 0.5 we see that all the KaK $\beta$  curves in <sup>2</sup>P cross the axis and then become negative. This negative behaviour when  $0 \leq z^{-1} p_{12} \leq 1$ 0.5 is in direct contrast with the <sup>2</sup>S behaviour in this region (except for Z=3 when we do note a small negative in the  $0 \leq z^{-1} p_{12} \leq 0.3$ ). These differences between <sup>2</sup>P and <sup>2</sup>S for KaK<sup> $\beta$ </sup> Coulomb shifts at small  $z^{-1}p_{12}$  are due to the differences in symmetry between the 2s and 2p orbitals. In the <sup>2</sup>S state, the Coulomb shift for KaKß will reflect the radial orthogonality property between the orbitals for the inner and outer shell. The 2s orbital will produce some confinement of the KaKB-shell and hence reduce radial correlation and consequently promote angular correlation. In the <sup>2</sup>P state, the angular orthogonality between the 1s and 2p orbitals allows the  $K \alpha K \beta$  Coulomb shift the ability to exercise radial correlation and therefore  $\Delta f(p_{12})$  can go negative at small  $z^{-1}p_{12}$  values. An overall measure of the

Coulomb shifts shown in Figure 3.1.13 may be obtained by inspection of the Y values, shown in Table 3.1.9 for  ${}^{2}P$  and Table 3.1.4 for  ${}^{2}S$ , and we note that the ordering of these values for KaK $\beta$  is Li( ${}^{2}P$ ) > Li( ${}^{2}S$ ) > Li<sup>+</sup>(1S) > Be<sup>+</sup>( ${}^{2}P$ ) > Be<sup>+</sup>( ${}^{2}S$ ) > Be( ${}^{1}S$ ).

Let us consider the  $g_{HF}(p_{12}, p_1)$  and  $\Delta g(p_{12}, p_1)$  surfaces for the KaK<sub>β</sub>-shell for Li, Be<sup>+</sup> and N<sup>4+</sup>. These surfaces are displayed in Figures 3.1.15(A) and 3.1.16(A) and display characteristics which are quite similar to those in <sup>2</sup>S, except when we consider  $\Delta g(p_{12}, p_1)$  at small  $p_1$  and small  $p_{12}$ . In <sup>2</sup>S we saw in  $\Delta g(p_{12}, p_1)$  a small positive effect at small  $p_1$  and  $p_{12}$ , whereas in the <sup>2</sup>P diagrams, we do not see it, due to the orthogonality condition between s and p orbitals. Consequently the  $\Delta g(p_{12}, p_1)$  surfaces for Li, Be<sup>+</sup> and  $N^{4+}$  are slightly more contracted towards the origin in  $^{2}$ P than those for  $^{2}$ S. Also we note that the magnitudes of positive and negative effects for <sup>2</sup>P in the partial Coulomb shifts are always slightly greater than the magnitude of the corresponding positive and negative effect in the <sup>2</sup>s surfaces. As 2 increases, the range of the  $\Delta g(p_{12}, p_1)$ values for the  $K\alpha K\beta$ -shell in <sup>2</sup>P is seen to decrease as  $-0.006 \leq \Delta g(Li) \leq +0.005, -0.0023 \leq \Delta g(Be^+) \leq +0.0019$  and  $-0.0004 \leq \Delta g(N^{4+}) \leq +0.0003$ , whereas in <sup>2</sup>S we found  $-0.006 \leq$  $\Delta g(Li) \leq +0.005$ ,  $-0.0017 \leq \Delta g(Be^+) \leq +0.002$  and  $-0.0002 \leq$  $\Delta g(N^{4+}) \leq +0.0003.$ 

In general, the  $\Delta g(p_{12}, p_1)$  surface for Be<sup>+</sup> for the K-shell appears to have two distinct but unequal regions. When 0.6  $\langle p_1 \rangle \langle 2.0$ , the sizeable negative region in the

surface clearly indicates the dominance of radial correlation. For  $P_1 > 2.0$ , angular correlation is now dominant. Radial and angular correlation are seen to have their maximum effects when the test electron has momentum values of about 1.4 and 3.4, respectively.

Figures 3.1.21(A) and 3.1.22(A) show the two-particle radial density  $D_{HF}(p_1, p_2)$  and the effect of correlation  $\Delta D(p_1, p_2)$  for the KaK<sub>β</sub>-shell, and Table 3.1.8 shows the HF and correlated expectation values  $\langle p_1^n p_2^n \rangle$ . The  $D_{HF}(p_1, p_2)$ and  $\Delta D(p_1, p_2)$  surfaces for Li, Be<sup>+</sup> and N<sup>4+</sup> possess features similar to those obtained for  $^2S$ , except when  $p_1$  is small and  $p_1 \approx p_2$ . The  $\Delta D(p_1, p_2)$ -surface in <sup>2</sup>S revealed a small positive density near the origin which is not observed in the <sup>2</sup>P-surface. For the KaK $\beta$ -shell, when  $p_1 * p_2$  and both values are small, it is reasonable to suppose that, in position space, the electrons will be located in the far outer regions of the shell and, as such, penetration into the L-shell region may well occur. With this in mind, it is interesting to note that, for  $^{2}$ P, where this small effect in  $\Delta D(p_1, p_2)$  is <u>absent</u>, an <u>angular</u> orthogonality exists between the K- and L-shell orbitals. This contrast between the K-shells for  ${}^{2}S$  and  ${}^{2}P$ , although small, is in keeping with a similar comparison between the  $\Delta g(p_{12}, p_1)$ -surface at small  $p_1 \approx p_{12}$ . The percentage change in  $\langle p_1^n p_2^n \rangle$  due to correlation reflects the influence of  $\Delta D(p_1, p_2)$  for the Li-like ions: the results are shown in Table 3.1.11.

### The Kala- and KBLa-Shells

Fot the inter-shells, the  $f_{HF}(p_{12})$  curves are well ordered when plotted against  $z^{-1}p_{12}$ . The  $f_{HF}(p_{12})$  vs  $z^{-1}p_{12}$ for a given 2 in  $^{2}$ P is slightly more diffuse than  $^{2}$ S and, hence, the maximum probability density of  $f_{HF}(p_{12})$  for <sup>2</sup>P is slightly less than for  $^2$ S. From Figure 3.1.11(B) we observe that the KaLa  $f_{HF}(p_{12})$ -curves show a flat region at small  $z^{-1}p_{12}$  which is due to the Fermi effect. Fermi correlation gives a zero value in <sup>2</sup>S for the two-particle density whenever  $|p_1| = |p_2|$  whereas in <sup>2</sup>P the density is zero only for the more limited condition represented by  $p_1 = p_2$ . For KaLa, the Coulomb shift in Figure 3.1.12(B) is negative at small  $2^{-1}p_{12}$  for each Z due to the presence of radial correlation. The crossovers of the  $\Delta f(p_{12})$  curves are located at values of  $z^{-1}p_{12}$  in the region of 0.5± 0.1 and 1.0 $\pm$ 0.2, whereas the Coulomb shifts in <sup>2</sup>S for the KaLa-shell have a major maximum and major minimum when  $2^{-1}p_{12}$  is about 0.5 and 1.0 (see Figure 3.1.2(B)). Also we note that the range of  $\Delta f(p_{12})$  for <sup>2</sup>P is from -0.0015 to +0.0011 whereas, for  ${}^2$ S, we have a range of -0.0006 to +0.00058. This is to be expected since, for <sup>2</sup>S, it is the outcome of the opposing effects of angular and radial correlation but for <sup>2</sup>P we have only radial correlation, as mentioned in the discussion of position space effects.

Consider now  $g_{HF}(p_{12},p_1)$  and  $\Delta g(p_{12},p_1)$  for the KaLashell. These densities are shown as surfaces in Figure 3.1.15(B) and 3.1.16(B). Since we are examining an intershell density we expect to see a diagonal and parallel

feature for  $g_{HF}(p_{12},p_1)$  in the KaLa-shell for a given Z. For Li it was found that  $g_{HF}(P_{12}, P_1)$  has two maxima whereas, for Be<sup>+</sup> and N<sup>4+</sup>,  $g_{HF}(p_{12}, p_1)$  is seen to have only one maximum although it has a diagonal and parallel structure, with these structures becoming less obvious as Z increases. This merging behaviour as Z increases was not seen in the  $^2$ S surfaces in momentum space. The  $g_{HF}(p_{12}, p_1)$  surfaces for <sup>2</sup>S always possessed distinct diagonal and parallel features for Li, Be<sup>+</sup> and N<sup>4+</sup> with each density having two maxima. This contrast in behaviour seems reasonable and in keeping with the one-particle radial densities in <sup>2</sup>S and <sup>2</sup>P for a given Z. From the one particle curves  $D_{HF}(p_1)$  (see Figure 3.1.23 and Table 3.1.7) we found that the ratio of  $p_{K}^{}/p_{L}^{}$  for <sup>2</sup>S is >5, >4 and  $\approx$ 4 for Z=3, 4 and 7, respectively, whereas for <sup>2</sup>P this ratio is  $\langle 4, \rangle \langle 3$  and  $\langle 2$  for Z=3, 4 and 7, respectively. This behaviour indicates that for the <sup>2</sup>S state the distinction between the  $p_{K}$  and  $p_{I}$  values is generally preserved as Z increases whereas, for  $^{2}p$ , the  $p_{K}$  and  $p_{T}$ values become closer in magnitude as Z gets larger. Consequently, the overlap of the diagonal and parallel features in the  $g_{HF}(p_{12}, p_1)$  surfaces in <sup>2</sup>P can produce a maximum which is greater than that located by either the  $p_{K}$ or p, values separately.

Let us now examine the effect of electron correlation on  $g(p_{12}, p_1)$  for the KaLa-shell for Li, Be<sup>+</sup> and N<sup>4+</sup>. The  $\Delta g(p_{12}, p_1)$  surfaces show a change from negative to positive as  $p_{12}$  increases when  $p_1$  is fixed equal to  $p_L$  which, for Li, Be<sup>+</sup> and N<sup>4+</sup>, has values 0.375, 0.75 and 1.95, respectively. This behaviour of  $\Delta g(p_{12}, p_1)$  implies an increase in the

momentum for the K-shell electron and is a consequence of the closer packing of the K-shell electron around the nucleus. This view is consistent with what we found in position space for the  $\Delta g(r_{12}, r_1)$  in <sup>2</sup>P for KaLa-shell. In position space we indicated that the diagonal positive density at  $r_{12} = r_1 \approx r_L$  was due to a radial correlation effect in the KaLa decription. An examination of  $\Delta g(p_{12}, p_1)$ for KaLa can also be made by fixing the test electron at large  $p_1 \approx p_K$ . For each Z we see a negative-positive effect as we cross the  $p_1=p_{12}$  diagonal axis. Since angular correlation is only a secondary effect, we suspect that this negative-positive behaviour in  $\Delta g(p_{12}, p_1)$  arises from an increase in the  $|p_L|$  magnitude. Clearly,  $g_{\rm HF}(p_{12}, p_1)$  and  $\Delta g(p_{12}, p_1)$  behave as  $f_{\rm HF}(p_{12})$  and  $\Delta f(p_{12})$ , respectively, when they are integrated with respect to  $p_1$ .

To study the partial Coulomb shift in more detail we calculated the density as a function of  $\theta_1$ , where  $\theta_1$  is measured relative to the symmetry axis of the system. Let us examine  $g_{HF}(p_{12},p_1,\theta_1)$  in the KaLa-shell for Z=3, 4 and 7. When  $\theta_1 = 90^\circ$  the test electron can be anywhere in the nodal plane of the 2p orbital and thus it can only be described by the K-shell orbital. Therefore, we expect  $p_1$  to be large which, in turn, will give rise to the diagonal effect in momentum space and no parallel effect. In position space for the corresponding surfaces we get only the parallel effect due to the reverse ordering in the extent of the 1s and 2p orbitals. At  $\theta_1 = 0^\circ$ , the test electron will be found on a line perpendicular to the nodal plane. Therefore,  $p_1$  can have a value corresponding either

to the K- or L-shell radius and thus we should see both diagonal and parallel effects in  $g_{\rm HF}(p_{12},p_1)$ . From Figure 3.1.17, we see that the diagonal effect is small compared with the parallel one. This is the reverse of the situation found in position space. The weak diagonal effect in momentum space is understandable since, when  $p_1 \approx p_K$  (i.e. large), we are confined to the unique line along the z-axis in the 1s shell and, therefore, the probability associated with this chosen value of  $p_1$  will be reduced. By contrast, when  $p_1 \approx p_L$  (i.e. small) the test electron is still located along the unique line but our restricted freedom is a closer representation of the 2p orbital symmetry and hence the consequence of such a restriction is less obvious.

Returning to Figure 3.1.17, selecting  $p_1 \approx p_K$  and  $\theta_1 =$ O' allows us to examine the L-shell density. Clearly, when  $P_{12}$  <  $P_K$  we are essentially sampling the upper lobe of the 2p-orbital and when  $p_{12} > p_{K}$  we are mainly sampling the lower lobe of the 2p-orbital. For the KaLa-shell we expect the Fermi effect to reduce the probability density when considering the upper lobe and, by comparison, to enhance the probability when sampling the lower lobe. When  $p_{12} =$  $P_{y}$ , the existence of the nodal plane in the 2p orbital produces a reduced probability density compared with the situations when  $p_{12} < p_K$  and  $p_{12} > p_K$ . Such behaviour shows itself in the appropriate g<sub>HF</sub>-surface as two maxima, of unequal heights, located either side of a reduced density along the  $p_{12} = p_1$  diagonal axis. However, when  $p_1 >> p_{\kappa}$  at  $\theta_1 = 0^{\circ}$ , the momenta of electrons 1 and 2 will be very different. Consequently, the Fermi effect produces less

distinction between the upper and lower lobes of the 2p-orbital and therefore the two maxima in the g<sub>HF</sub>-surface, although of smaller magnitude, will be almost equal in size and location with respect to the diagonal axis. As Z increases, the L shell moves, in position space, towards the nucleus and thus its momentum gets closer to the K-shell value. Therefore, when the test electron has a value of  $p_1$  $\approx$  p<sub>K</sub>, the individual p-orbital lobes will be shown more clearly over a greater range of  $p_1$  (where  $0 < p_1 < p_k$ ). Nevertheless, at  $\theta_1 = 0^\circ$ , the main feature shown by the  $g_{HF}$ surfaces is, of course, still the parallel one when  $p_1 \approx p_L$ . Consequently, if p, is reduced in magnitude from a value p, > p<sub>k</sub>, we see that the density on the left-hand side of the diagonal becomes smaller than that on the right-hand side. This result is due to the Fermi effect between the test electron (when  $\theta_1 = 0^\circ$ ) and the upper lobe of the 2p-orbital The  $g_{HF}(p_{12}, p_{1}, \theta_{1}=30^{\circ})$  for the momentum space. in KaLa-shell shows a similar behaviour to  $g_{HF}(p_{12}, p_1, \theta_1=0^*)$ when the test electron is placed at  $p_1 \approx p_K$ , but at  $\theta_1=30^{\circ}$ Fermi correlation is less effective. Therefore when  $\theta_1 = 60^{\circ}$ the  $g_{HF}(p_{12}, p_{1}, \theta_{1})$  looks rather like the integrated  $g_{HF}(p_{12}, p_1)$ .

Having understood the behaviour of the  $g_{HF}(p_{12}, p_{1}, \theta_{1})$ density for the KaLa-shell, let us now consider the effect of correlation. From Figure 3.1.19, we see that the features in the  $\Delta g(p_{12}, p_{1}, \theta_{1})$  surfaces behave as follows: as  $\theta_{1}$  increases from 0° to 90° the diagonal feature becomes emphasized in momentum space and the parallel feature is reduced. At  $\theta_{1}=0^{\circ}$  the  $\Delta g(p_{12}, p_{1}, \theta_{1})$  surface shows a

negative-positive effect relative to the diagonal density in the HF surface; the effect is most noticeable when  $P_1 \approx P_K$ . This might be interpreted as an increase of L-shell momentum. The major feature of the  $\Delta g(P_{12}, P_1, \theta_1)$  surface when  $\theta_1=0^\circ$  is seen to be parallel to the  $P_{12}$  axis and is located around  $P_1 \approx P_L$ . We note that, for any given  $P_{12}$ , the parallel feature behaves as a negative-positive effect as  $P_1$  increases from zero to a value mid-way between  $P_L$  and  $P_K$ . At  $\theta_1=90^\circ$ , the KaLa  $\Delta g(P_{12}, P_1, \theta_1)$  surfaces show the diagonal feature only. This implies that we have a K-shell test electron and an L-shell response to correlation.

Consider now  $D_{HF}(p_1, p_2)$  and the  $\Delta D(p_1, p_2)$  for the KaLa-shell shown in Figures 3.1.21(B) and 22(B) for Li, Be<sup>+</sup> and N<sup>4+</sup>. The HF surface shows features similar to those for the KaLa-shell in <sup>2</sup>S except in a small region when  $p_1 \approx p_2 \approx$  $p_L$ . In this region  $(p_2=p_1=p_L)$ ,  $D_{HF}(p_1,p_2)$  for <sup>2</sup>P is nonzero, in contrast to the corresponding density in  $^2$ S. The  $D_{HF}(p_1,p_2)$  diagrams for KaLa in the <sup>2</sup>P state show that as Z increases the density in this region increases. For Li and Be<sup>+</sup> we see that, as for  ${}^{2}S$ , the D<sub>HF</sub>( $p_{1}, p_{2}$ )-densities possess two maxima corresponding to two distinct regions of density whereas, for  $N^{4+}$ , there is one maximum density located on the diagonal  $(p_2=p_1=p_1)$ , a result which contrasts with that for the <sup>2</sup>S state. The changes in the two-particle densities are shown by  $\Delta D(p_1, p_2)$ . The  $\Delta D(p_1, p_2)$  surfaces indicate that the density has moved from low  $p_1$  to high  $p_1$ . As expected from the  $D_{HF}(p_1, p_2)$  surfaces, the diagonal feature in  $\Delta D(p_1, p_2)$  is quite different from that in <sup>2</sup>S. As 2 increases the AD diagrams reveal different behaviour

corresponding to that already observed for the HF surfaces. The change in the  $D_{HF}(p_1,p_2)$  densities due to correlation produce the percentage changes in  $\langle p_1^n p_2^n \rangle$  shown in Table 3.1.11.

The electron correlation for the KBLa-shell can be studied in the same way as for the KaLa-shell. The  $f_{HF}(p_{12})$ vs  $2^{-1}p_{12}$  are displayed in Figure 3.1.11(C) and this function shows similar trends with repect to 2 as was found for the KaLa-shell. The comparison between KBLa and KaLa for  $f_{HF}(p_{12})$  shows that the  $f_{HF}(p_{12})$  for a given Z has a maximum which is less than that in KaLa. The Coulomb shift for the KBLa-shell shows a sharp drop as the curve moves away from the origin; this is in contrast to the small flat region in the KaLa caused by the Fermi effect. From the K $\beta$ L $\alpha$  curves we see, roughly speaking, that  $\Delta f(p_{12})$  has a negative - positive behaviour with repect to increasing  $z^{-1}p_{12}$ . However, for KaLa we saw that  $\Delta f(p_{12})$  behaves, roughly, as a negative -positive and negative curve with repect to increasing  $2^{-1}p_{12}$ . Figure 3.1.14 shows the relative magnitudes of the KaLa- and KBLa-Coulomb holes for Li, Be<sup>+</sup> and N<sup>4+</sup> as well as the K $\alpha$ K $\beta$ - and total holes. The effect of Coulomb correlation in KBLa is seen to be greater that that in the KaLa-shell, a result which is not unreasonable in view of the presence of Fermi correlation in the KaLa-shell. A similar result was found for the inter-shells in <sup>2</sup>S.

A comparison between the normalized total Coulomb shifts for  ${}^2p$  and  ${}^2S$  shows that, at small  $2^{-1}p_{12}$ , the influence of

the inter-shells is quite different for the states. The  ${}^{2}P$  curves contain less structure than those for  ${}^{2}S$ . In passing, we note that when  ${}^{2-1}p_{12} > 1$ , both sets of normalized total shifts are dominated by the K $\alpha$ K $\beta$  shell and hence exhibit a high degree of similarity. This is understandable since, in Li, the electrons in the K and L-shells will have different momenta and hence Fermi correlation in K $\alpha$ L $\alpha$  has a comparatively small effect and therefore a large similarity should exist with K $\beta$ L $\alpha$  for Z=3. At Z=7, the K and L-shell electrons not only have greater momenta than was the case in Li but their values are now closer in magnitude and hence the Fermi effect has a greater effect. Consequently, at small  $p_{12}$ , the differences between  $g_{\rm HF}(p_{12}, p_1)$  for K $\alpha$ L $\alpha$  and K $\beta$ L $\alpha$  in N<sup>4+</sup> are much more noticeable.

Consider the partial Coulomb shifts for the KBLa-shell as shown in Figure 3.1.16(C) for Li,  $Be^+$  and  $N^{4+}$ . When  $p_1$ and  $p_{12}$  are both small, we see a negative region which is more extensive and deeper than that in the KaLa case for  $^{2}$ P. This behaviour is particularly obvious for  $N^{4+}$  where the negative in KBLa is almost twice as deep as in KaLa. The effect is most noticeable for Z=7 since the large nuclear charge causes a merging of the K and L-shells (it was noted in position space that, generally, the L-shell contracted more rapidly than the K-shell as Z increased in value). The above effect is still obvious for Z=4 but is much less clear cut for Z=3. Generally, at  $p_1 \approx p_1$ , we see a negativepositive effect with repect to increasing p<sub>12</sub>, and this agrees with our KaLa findings and also agrees with our position space observations. When the test electron has

 $p_1 \approx p_K$  the  $\Delta g(p_{12}, p_1)$  surfaces for K  $\beta L \alpha$  shows the influence of electron correlation as a negative - positive feature as  $p_{12}$  increases. This indicates an increase in the L-shell momenta which, in turn, is compatible with the inward movement of the L-shell density observed in position space.

As for the KaLa-shells, we now examine the Coulomb shifts for  $K\beta L\alpha$  as a function of  $p_1$  and  $\theta_1$ . The results for  $g_{HF}(p_{12}, p_1, \theta_1)$  and  $\Delta g(p_{12}, p_1, \theta_1)$  for Li, Be<sup>+</sup> and N<sup>4+</sup> are presented in Figures (3.1.18 and 3.1.20). For  $\theta_1=0^{\circ}$ , 30°, 60°, and 90°,  $g_{HF}(p_{12}, p_1, \theta_1)$  for K $\beta$ La shows, in general, similar patterns of behaviour as was found for KaLa, with exceptions occurring when  $\theta_1 = 0^\circ$  and  $30^\circ$ , for  $p_1 \approx p_K^\circ$ . The KaLa discussion for  $g_{HF}(p_{12}, p_1, \theta_1)$  can be used here. For the surfaces when  $\theta_1 = 0^\circ$  and 30°, we see that when  $p_1 \approx p_K$  a maximum occurs on both sides of the diagonal axis and, unlike the KaLa-shell, these maxima for KBLa are of comparable magnitude. This contrast in behaviour between the  $g_{HF}(p_{12}, p_1, \theta_1=0^{\circ})$  surfaces for KBLa and KaLa is clearly obvious when comparing Figure 3.1.18 with Figure 3.1.17. As in the KaLa-shell, the diagonal and parallel features in the  $g_{\rm HF}$  surfaces behave differently from each other as  $\theta_1$ increases. When  $\theta_1 = 90^\circ$ , we see only a diagonal effect in the  $g_{HF}(p_{12}, p_1, \theta_1)$  density. The  $\Delta g(p_{12}, p_1, \theta_1)$  surfaces for the KßLa-shell shown in Figure 3.1.20 reveal the influence of correlation effects in  $g_{HF}(p_{12}, p_{1}, \theta_{1})$ . From these diagrams, when  $\theta_1 = 0^{\circ}$  and  $30^{\circ}$ , the test electron can be in the L-shell (mostly) when  $p_1 \approx p_L$  and so we are examining the K-shell. From  $\theta_1=0^{\circ}$  the  $\Delta g(p_{12}, p_1, \theta_1)$  surface shows, as expected, a negative - positive effect on the K-shell shift

as  $p_{12}$  increases. Now if we keep  $p_1 \approx p_L$ , but let  $\theta_1$ increase to 90° then even though  $p_1 \approx p_L$  the test electron is now in the K-shell (since the L-shell orbital is zero in its nodal plane) with a much reduced probability. Consequently, the variation of  $\Delta g$  with repect to  $p_{12}$ corresponds to a correlation shift for the L-electron. This effect on the L-shell is again seen to be negative positive as  $p_{12}$  increases but the negative and positive regions are now only about one-sixth of the size of the  $\theta_1=0^\circ$  values for the same small  $p_1 = |p_L|$  value. Like the KaLa shell, the integrated effect  $\Delta g(p_{12}, p_1)$  seems to have characteristics which are similar to those for the  $\Delta g(p_{12}, p_1, \theta_1)$  surface when  $\theta_1=60^\circ$ .

Finally, let us examine the  $D_{HF}(P_1,P_2)$  and the  $\Delta D(P_1,P_2)$ surfaces for the K $\beta$ L $\alpha$ -shell. Figures 3.1.21-22(C) show the  $D_{HF}(P_1,P_2)$  and  $\Delta D(P_1,P_2)$  surfaces for Li, Be<sup>+</sup> and N<sup>4+</sup>. The HF surfaces show features identical to those for the K $\alpha$ L $\alpha$ -shell whereas, in <sup>2</sup>S, these densities are not equal due to the presence of the Fermi effect in the K $\alpha$ L $\alpha$ -shell. A similar observation was made in position space. The  $\Delta D(P_1,P_2)$  surface for Li in the K $\beta$ L $\alpha$ -shell shows that the correlation effects are the same as for the K $\alpha$ L $\alpha$ -shell. As z increases a comparison of the  $\Delta D$ -surfaces for the K $\alpha$ L $\alpha$ and K $\beta$ L $\alpha$ -shells reveals different behaviours in the two shells. For the K $\beta$ L $\alpha$ -shell, the  $\Delta D$  diagrams indicate a significant movement of the density from low  $P_1$  to high  $P_1$ compared to that found for the K $\alpha$ L $\alpha$ -shell.

## CHAPTER 3.1.5

#### SUMMARY

The correlation effects in momentum space are analyzed and compared within the individual electronic shells for a series of Li-like ions in the <sup>2</sup>S- and <sup>2</sup>P-states. This was achieved by means of a partitioning technique used previously in position space. In momentum space, we have examined the  $\Delta f(p_{12})$ -curves, which are particularly useful since the structure of such Coulomb shifts reflects the nature of the dominant correlation component for a given electronic shell. This behaviour is in contrast with that found earlier in position space<sup>(81)</sup>, where radial and angular correlation effects reinforce each other. Banyard and Moore<sup>(81)</sup> established that, in momentum space, the radial correlation coefficients for two-electron ions are negative, as in position space, whereas, by contrast, the angular coefficients are positive. Therefore, for the momentum distribution  $f(p_{12})$ , the effect of total correlation creates changes which are considerably more complex than those which arise in position space.

The Coulomb shifts for  ${}^{2}S$  and  ${}^{2}P$  in the KaK $\beta$ -shell show a high degree of similarity for the Li-like ions when  ${z^{-1}p}_{12}$ > ,0.5 and both states show the domninance of angular correlation in the KaK $\beta$ -Coulomb shifts. In the region when 0 <  ${z^{-1}p}_{12}$  < 0.5, the KaK $\beta$ -curves show significant differences between the  ${}^{2}S$ - and  ${}^{2}P$ -states. For the  ${}^{2}P$  state, the radial component of electron correlation gives rise to negative values for  $\Delta f(p_{12})$  which are very similar to the

ionic curves obtained by Reed<sup>(77)</sup> for two-electron systems. However, for <sup>2</sup>S, when  $Z^{-1}p_{12} < 0.5$ , the  $\Delta f(p_{12})$  curves for Be<sup>+</sup>, B<sup>2+</sup>, N<sup>4+</sup> and 0<sup>5+</sup> give a positive value which is a consequence of angular correlation. The above findings are in general accord with a comparison between the corresponding  $\Delta \tau$  values. It was found, for example, that the  $\Delta \tau_{1/p}$  values for KaK $\beta$  are ordered in magnitude as Be(<sup>1</sup>S) << Be<sup>+</sup>(<sup>2</sup>S) << Be<sup>2+</sup>(<sup>1</sup>S) < Be<sup>+</sup>(<sup>2</sup>P). Therefore, by comparision with Be<sup>2+</sup>, radial correlation at small momenta in the Be<sup>+</sup> and Be K-shells is inhibited by the presence of the one and two L-shell electrons respectively. As a consequence of different symmetry of the 2s and 2p orbitals in the Li-like ions, we expect a different behaviour between the <sup>2</sup>S- and <sup>2</sup>P-states for the Coulomb shifts at small p<sub>12</sub>. This was indeed the case.

For the inter-shells, comparisons can be made of the  $f_{\rm HF}(P_{12})$  and  $\Delta f(P_{12})$ -curves for the Li-like ions between the  ${}^{2}S$  and  ${}^{2}P$  states. At small  $P_{12}$ , the KaLa curves for both states give a flat region due to the presence of the Fermi effect. Fermi correlation gives a zero value in  ${}^{2}S$  for the two-particle density whenever  $|P_{1}| = |P_{2}|$  whereas, in  ${}^{2}P$ , the density is zero only for the more limited condition represented by  $P_{1} = P_{2}$ . Consequently, when adding Coulomb correlation into the description, it is not surprising that its influence in the  ${}^{2}S$  state is considerably less important than in  ${}^{2}P$ . The effects of Coulomb correlation in  ${}^{2}S$  are smaller than in  ${}^{2}P$ . This finding, in momentum space, is also supported by the inspection of the Y\* values. The results for  ${}^{2}S$  are smaller than the Y\* values for  ${}^{2}P$  in each

individual electronic shell. As in the He-like ions, we found that the momentum results for Y are smaller than those in position space for both  $^2$ S and  $^2$ P. In momentum space for both states, the effects of Coulomb correlation in the K $\beta$ L $\alpha$ -shell are greater than in K $\alpha$ L $\alpha$ , a result which is not unreasonable in view of the presence of Fermi correlation in K $\alpha$ L $\alpha$ .

Further points of contrast between the S and P states can be seen from the normalized total  $\Delta f(p_{12})$  at  $0 < z^{-1}p_{12}$  $\leq$  0.5. The <sup>2</sup>P curves show a negative region whereas, in <sup>2</sup>S, although the curves are identically negative at small  $z^{-1}p_{12}$ (but of smaller magnitude than for the <sup>2</sup>P-state) they have all become positive when  $Z^{-1}p_{12} > 0.25$ . In general, the difference in behaviour of  $\Delta f(p_{12})$  between the <sup>2</sup>P and <sup>2</sup>S curves is due to the different behaviour of the inter-shells in both states. These observations are understandable in view of the absence of direct angular correlation in the <sup>2</sup>P wavefunction. The  $\Delta f(p_{12})$  curves for the KaK<sub>β</sub>-shell and the normalized total effect for the both states show a common crossover point at  $z^{-1}p_{12} = 1.5$ . Clearly as in position space for the Li-like ions, the normalized total curves for the both states show the dominance of the effect of the K $\alpha$ K $\beta$ Coulomb shift. In momentum space, the effect is located at large  $p_{12}$  whereas, in position space, it is located at small r<sub>12</sub>.

The Coulomb shift has been studied as a function of  $p_1$ by the determination of the partial Coulomb shifts  $\Delta g(p_{12}, p_1)$  in <sup>2</sup>S and <sup>2</sup>P for individual electronic shells.

For the KaK<sub>β</sub>-shell, the  $\Delta g(p_{12}, p_1)$  surfaces in <sup>2</sup>p show characteristics which are much the same as for those in  $^2S$ except at small  $p_1$  and small  $p_{12}$ . In the <sup>2</sup>S state we saw a small positive effect for the  $K\alpha K\beta$ -shell for Li, Be<sup>+</sup> and  $N^{4+}$ , whereas in <sup>2</sup>P, the KaKß surfaces did not show this positive effect at small p<sub>1</sub> and small p<sub>12</sub>. This contrast between P and S states is in keeping with the behaviour of the Coulomb shift  $\Delta f(p_{12})$  at small  $p_{12}$  and is also in accord with the change in the  $\tau$  values. The cause of this positive  $\Delta g$  at small  $p_1$  and  $p_{12}$  is perhaps due to the effect of integrating out the L-shell electron when partitioning the two-particle density. Therefore it was anticipated that this feature would not appear in the <sup>2</sup>P state because of the orthogonality condition between the s and p orbitals. Our results confirmed this conjecture. In position space, the KaKB-diagrams of the partial Coulomb holes for both states show almost identical characteristics. We note that, in momentum space, the  $\Delta g(p_{12}, p_1)$ -surfaces for the KaK $\beta$ -shells • for Li, Be<sup>+</sup> and N<sup>4+</sup> in <sup>2</sup>P are slightly more contracted towards the origin than those for  $^2$ S, and also we found that the magnitude of the positive and negative effects for <sup>2</sup>P are always slightly greater than those characteristics in the <sup>2</sup>S surfaces. Otherwise, the  $\Delta g(p_{12}, p_1)$  surfaces showed features similar to those obtained for the corresponding density in <sup>2</sup>S, and therefore emphasise once again, that radial and angular correlation produce effects in the KαKβ-shell which are common to both states. However, contrary to the findings in position space as Z increased, the surfaces not only became more diffuse but also decreased in magnitude.

For the inter-shells, the g<sub>HF</sub>(p<sub>12</sub>,p<sub>1</sub>) surfaces show diagonal and parallel characteristics and their extent reflects the spread of the K- and L-shell densities respectively. In position space, the diagonal and parallel characteristics in those surfaces are such that, in this space their spread now reflects that of the L- and K-shells densities. The inversion of these diagonal and parallel features for both spaces is due to the reverse ordering in the extent of the 1s and 2p orbitals. The comparision between the  $g_{\rm HF}^{}$ -surfaces in the inter-shells for the <sup>2</sup>S and <sup>2</sup>P states show obvious differences due to the different symmetry of the outer orbital. This contrast is in accord with the one-particle density, which is a result of integrating the  $g_{HF}(p_{12}, p_1)$  density with respect to  $p_{12}$ . The comparison between the KaLa- and KBLa-shells for  $g_{HF}(p_{12}, p_1)$  for both states shows a difference at small  $p_{12}$ for Li,  $Be^+$  and  $N^{4+}$ .

Due to the Fermi correlation in the KaLa-shell, a difference between the KaLa and K $\beta$ La-shell for the  $\Delta g(p_{12}, p_1)$ -surfaces can be found at small  $p_{12}$ . As we examine  $\Delta g(p_{12}, p_1)$  for each Z at chosen  $p_1 \approx p_L$  values we see that as  $p_{12}$  increases from zero to a large value then, for that fixed  $p_1$  value, the sign of the  $\Delta g$ -surface changes from negative (at small  $p_{12}$  values) to positive (at large  $p_{12}$  values). This occurs for Li, Be<sup>+</sup> and N<sup>4+</sup> for the KaLa and K $\beta$ La-shells in the  $^{2}P$  state. This similarity in  $^{2}P$  between KaLa and K $\beta$ La also occurred for Li in  $^{2}S$  but not for Be<sup>+</sup> and N<sup>4+</sup>. For  $p_1 \approx p_K$ , the  $\Delta g(p_{12}, p_1)$  surfaces in  $^{2}p$ 

for KaLa- and KBLa show a negative-positive effect which occurs as  $p_{12}$  increases. This is in contrast with the inter-shell diagrams in <sup>2</sup>S which show a positive-negative effect when  $p_1 \approx p_K$  as  $p_{12}$  increases. For the <sup>2</sup>S and <sup>2</sup>p states, the KBLa partial Coulomb shifts show a significant negative at small  $p_{12}$  and small  $p_1$  which did not exist in the KaLa-diagrams due to the presence of the Fermi effect.

Further investigation was made by studying the partial Coulomb shift in  ${}^{2}P$  for the inter-shells as a function of  ${}^{0}_{1}$ , where  ${}^{0}_{1}$  was measured relative to the symmetry axis of the system.

Examination of the two-particle radial density for KaK $\beta$ shows a high degree of similarity between  ${}^2S$  and  ${}^2P$  in both position and momentum spaces. The  $\Delta D(p_1, p_2)$  surfaces for Li, Be<sup>+</sup> and N<sup>4+</sup> showed features similar to those obtained for the corresponding density in  ${}^2S$ , except at small  $p_1$  and small  $p_2$ . In the  ${}^2P$ -state, the KaLa-shell  $D_{\rm HF}$  surface for a given atom is equal to that for the K $\beta$ La-shell, whereas, in  ${}^2S$ , these densities are not equal due to the presence of the Fermi effect in the K $\alpha$ La-shell. In both position and momentum space the comparison between the  $\Delta D$ -surfaces for K $\alpha$ L $\alpha$  and K $\beta$ L $\alpha$  shows that correlation effects are not the same on the diagonal axis in  ${}^2S$  and  ${}^2P$ . This is not unreasonable in view of the behaviour of the HF surfaces.

Tables and Figures for the <sup>2</sup>S-states

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			6	5	<u>ו</u> ת	9	6	יינ	· ~	æ	7	> ~	1 10	-		0 4	0 0	6			0.0	6	ך נ	7	1
P12	)	CORR	1.821	1.433	1.478	1.643	2 452	1 823	2.008	2.183	3 060	0.000	2.504	2.734		- 4/4- 0 - 4/0	3.7265	4.029	5 1213	3.9456	4.3156	4.6085	dividua	derive	
		HF	1.8931	1.4301	1.4810	1.6763	2 5226	1.8204	2.0128	2.2175	3 1253	2 3212	2.5082	2.7653	CC04 4		3.7345	4.0195	5 1899	3.9408	4.3244	4.6421	the in	ilts are	
	2	CORR	13.8041	7.5820	7.5387	9.6416	25.8917	14.2575	14.5833	18.2442	41 5231	23.8451	23.6989	29.6890	85 9041	50.0850	51.0671	63.0855	14.3087	68.6396	68.3581	83.7688	state foi	these resu	
	"	HF	14.4233	7.5632	7.5553	9.8473	26.7621	14.2341	14.6274	18.5411	42.5972	23.8110	23.7603	30.0562	87 5253	51 1922	51.2151	63.3109	16.2057	68.5710	68.5485	84.4417	$(1s^{2}2s)^{2}S$	e ions. 1	
n, , , , , , , , , , , , , , , , , , ,	-	CORR	3.2384	2.3511	2.3137	2.6344	4.4585	3.3063	3.2478	3.6709	5.6710	4.2940	4.1745	4.7131	8,1441	6.2922	6.0974	6.8446	9.3851 1	7.2849	7.0522	7.9074	for the	che Li-lik	unctions.
4	" "	HF	3.2923	2.3490	2.3156	2.6528	4.5165	3.3046	3.2521	3.6910	5.7297	4.2922	4.1796	4.7338	8.2064	6.2896	6.1048	6.8669	9.4483	7.2829	7.0603	7.9305	operties	ues for t	HF Wavel
-	- 1 R	CORR	0.4281	0.5749	0.6340	0.5457	0.3103	0.3949	0.4480	0.3844	0.2432	0.3006	0.3463	0.2967	0.1694	0.2035	0.2375	0.2035	0.1471	0.1753	0.2053	0.1759	tion pro	otal val	eiss <sup>(26)</sup>
	5	HF	0.4256	0.5753	0.6338	0.5449	0.3083	0.3949	0.4478	0.3837	0.2418	0.3006	0.3462	0.2962	0.1687	0.2035	0.2375	0.2032	0.1465	0.1753	0.2053	0.1757	expecta	alized T	CI and W
1p2 >	0 = u	CORR	0.3160	0.0060	0.0058	0.1092	0.4472	0.0167	0.0162	0.1600	0.5794	0.0279	0.0270	0.2114	0.8430	0.0511	0.0505	0.3148	0.9744	0.0625	0.0612	0.3660	article	the norm	i <b>ss</b> (25)
ם <sub>1</sub> .פעום	n = 1	CORR	0.0377	0.0058	0.0042	0.0159	0.0283	0.0064	0.0051	0.0133	0.0227	0.0058	0.0047	0.0111	0.0161	0.0046	0.0039	0.0082	0.0141	0.0041	0.0035	0.0072	ae two-r	ells and	using We
~	n = 2	CORR	0.0083	6700.0	0.0083	0.0080	0.0033	0.0034	0.0042	0.0036	0.0016	0.0017	0.0022	0.0018	0.0006	0.0006	0.0008	0.0004	0.0004	0.0004	0.0005	0.0004	1.1 Som	she	γd
	SHELL		Ka KB	NA LO	D I I I	Total	KaKB	Kala	KBLQ	Total	K aK B	KaLa	KB La	Total	KaKß	Ka La	KB La	Total	KαKβ	Ka La	KBLO	Total	ble 3.		
	8			ſ	n			•	4			1	ŝ				~			c	Ø		13		

			1		1			_			1		л t
P1		CORR	1.478 1.435 1.432	1.511	2.005 1.945	2.038	2.532 2.462 2.454	2.570	3.588 3.497 3.489	3.639	4.116 4.021 4.009	4.176	2s sta
41/		ΗF	1.476 1.433	1.510	2.004 1.941	2.038	2.531 2.457	2.570	3.588 3.494	3.639	4.116 4.014	4.175	1s <sup>2</sup> 2s)
P1		CORR	0.576 2.753 2.565	2.322	0.414 1.582 1.582	1.375	0.323 1.121 1.121	0.975	0.224 0.713 0.713	0.620	0.194 0.604 0.604	0.525	r the
Φ		HF	0.577 2.777	2.413	0.415 1.589	1.381	0.323 1.123	0.977	0.224 0.712	0.620	0.194 0.603	0.525	<b>Δ1/p</b> fo
	2	CORR	7.229 3.837 3.822	4.962	13.576 7.521 7.489	9.526	21.923 12.462 12.391	15.591	<b>44</b> .612 26.099 25.968	32.227	58.960 34.797 34.632	42.796	P, and
	" 2	HF	7.224 3.821	4.955	13.575 7.489	9.518	21.923 12.414	15.584	44.614 26.019	32.217	58.958 34.697	42.784	ations <b>D</b>
•		CORR	2.2461 1.3332 1.3309	1.6367	3.0917 1.9330 1.9284	2.3177	3.9384 2.5301 2.5241	2.9975	5.6337 3.7240 3.7144	4.3574	6.4819 4.3165 4.3082	5.0355	ard devi
₽1 >	1	HF	2.2460 1.3298	1.6352	3.0921 1.9288	2.3165	3.9389 2.5255	2.9966	5.6340 3.7165	4.3557	6.4820 4.3115	5.0330	he stand
~ .	+-	CORR	0.6570 2.2453 2.2455	1.7159	0.4744 1.3375 1.3378	1.0499	0.3711 0.963 <b>4</b> 0.9636	0.7659	0.2583 0.6218 0.6219	0.5007	0.2243 0.5288 0.5289	0.4273	> and t
	ו ע	HF	0.6571 2.2612	1.7265	0.4744 1.3418	1.0527	0.3711 0.9648	0.7669	0.2584 0.6219	0.5007	0.2243 0.5287	0.4272	ues <p<sup>2</p<sup>
	·2	CORR	0.7634 2.6209 1.6195	8.3346	0.3962 4.2931 4.2922	2.9938	0.2418 2.1856 2.1851	1.5375	0.1168 0.8947 0.8944	0.6353	0.0880 0.6442 0.6440	0.4587	tion val
		HF	0.7644 2.8262 1	8.8056	0.3969 4.3251	3.0157	0.2421 2.1926	1.5424	0.1169 0.89 <b>4</b> 3	0.6352	0.0880 0.6432	0.4581	Expectat
	SHELL		Ka KB Ka La KB La	Total	KaK A Ka La KB La	Total	ΚαΚβ Κα Lα Κβ Lα	Total	KaK A Ka La Kb La	Total	KaK B Ka La KB La	Total	le 3.1.2
	8		e e e	-	4	-	ŝ		~		8	-	Tabi

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for the individual shells and the normalized Total values for the Li-like ions. The results are derived by using Weiss<sup>(25)</sup> CI and Weiss<sup>(26)</sup> HF wavefunctions.

	-								
	1				< p <sup>n</sup>	p2 >			5
2	SHELL	H	-2	n £		1 L	-	E	= 2
		HF	CORR	HF	CORR	HF	CORR	HF	CORR
	Κα Κβ	0.5843	0.5821	0.4318	0.4260	5.0446	4.9152	52.1836	46 0634
, 	Kala	12.0109	11.7542	2.3057	2.2827	0.7804	0.7869	1.0708	1.0879
<b>n</b>	KB LO	19.0239	18.6072	2.5400	2.5181	0.9290	0.9334	3.6163	2.9018
	Total	10.5397	10.3145	1.7591	1.7423	2.2514	2.2118	18.7569	16.6843
	K aK B	0.1576	0.1582	0.2251	0.2234	9.5668	9 3967	184 2768	TC11 031
	KaLa	1.8575	1.8361	0.9205	0.9156	1.8961	1.9054	6.0854	6 1585
4	KBLa	3.2760	3.2258	1.0481	1.0434	2.3670	2.3630	19.0579	18.2415
	Total	1.7637	1.7401	0.7312	0.7275	4.6080	4.5550	69.8067	64.6046
	K aK B	0.0586	0.0590	0.1377	0.1370	15.5148	15.3172	480 6013	451 2890
1	KaLa	0.5407	0.5373	0.5000	0.4984	3.4413	3.4531	19 6606	19 8516
<u>ب</u>	KB La	1.0031	0.9922	0.5784	0.5769	4.3803	4.3646	63.6949	61.1978
	Total	0.5342	0.5295	0.4054	0.4041	7.7788	7.7116	187.9856	177.4461
	KαKβ	0.0137	0.0138	0.0668	0.0666	31.7423	31 4811	1990 2065	10/0 57/5
(	KaLa	0.1004	0.1002	0.2107	0.2165	7.8325	7.8504	126.99.92	100 6170 001
<u> </u>	KBLa	0.1955	0.1943	0.2546	0.2544	10.1355	10.1054	331.1898	320.6896
	Total	0.1032	0.1028	0.1794	0.1791	16.5701	16.4790	807.1745	776.9591
	KaKB	0.0077	0.0078	0.0503	0.0502	42.0167	41.7267	3476.0971	3355.9629
~	Kala	0.0535	0.0534	0.1584	0.1583	10.6797	10.6954	184.8253	185.8985
>			0601.0	0.1868	0.1868	13.8775	13.8155	615.2809	597.4350
	Total	0.0556	0.0554	0.1318	0.1318	22.1913	22.0792	1425.4011	1379.7654
Tab	le 3.1.3	Expectat	ion value	< < b <sup>1</sup> <sub>2</sub> b <sup>2</sup>	for the (	1s <sup>2</sup> 2s) <sup>2</sup> S s	tate for t	he individua	l shells and
		the nor	rmalized T	otal valu	tes for t	che Li-like	ions. Th	e results ar	e derived hv
		using We	iss <sup>(25)</sup> CI	and Weiss	(26) HF Wa	vefunction	ŝ		

2	SHELL	Δτ	Δτ <sub>1/P</sub>	۵۲۲	Δτ <sub>Υ</sub> .	Δτ <sub>γ</sub>	۶
e	KαKβ KαLα Kβlα Total	-0.05931 +0.00038 +0.00031 -0.01927	-0.01747 +0.00008 -0.04989 -0.01327	+0.04371 +0.00156 +0.00151 +0.02202	+0.01084 +0.00060 +0.00071 +0.00096	+0.03772 +0.00579 +0.00421 +0.01591	1.1294 0.0914 0.1589
4	KαKβ KαLα KβLα Total	-0.04024 +0.00016 -0.00154 -0.01392	-0.00952 -0.00028 -0.00021 -0.00058	+0.03294 +0.00222 +0.00216 +0.01680	+0.00827 +0.00079 +0.00097 +0.00120	+0.02833 +0.00636 +0.00508	0.8549 0.0792 0.1666
Ś	KαKβ KαLα KβLα Total	-0.03022 +0.00011 -0.00230 -0.01090	-0.00629 -0.00019 -0.00007 -0.00045	+0.02643 +0.00224 +0.00218 +0.01356	+0.00667 +0.00076 +0.00099 +0.00118	+0.02268 +0.00576 +0.00473 +0.01106	0.6856 0.0726 0.1518 0.2141
~	KαKβ KαLα KβLα Total	-0.02000 -0.05290 +0.00625 -0.02079	-0.00359 -0.00001 -0.00046 -0.00044	+0.01890 +0.00196 +0.00194 +0.00194	+0.00479 +0.00065 +0.00088 +0.00088	+0.01615 +0.00458 +0.00389 +0.00389	0.4848 0.0582 0.1256 0.1633
œ	KαKβ KαLα KβLα Total	-0.01703 -0.00001 -0.00275 -0.00412	-0.00292 +0.00004 -0.00049 -0.00297	+0.01653 +0.00180 +0.00177 +0.00855	+0.00420 +0.00059 +0.00080 +0.00080	+0.01412 +0.00409 +0.00346 +0.00722	0.4329 0.0483 0.1148 0.1464
Tab.	le 3.1.4	The change $\Delta t$	in the re	dial and and			

radial and angular correlation coefficients  $\tau$  for the  $(1s^2 2s)^2 s$  state for the individual electronic shells in the Li-like ions. Also listed is Y - the percentage of the interparticle momentum distribution function  $f_{HF}(P_{12})$  which has been re-distributed due to electron correlation.

		U •	hange in <p< th=""><th>n 12<sup>&gt;</sup></th><th><b>6</b></th><th>:hange in &lt;₁</th><th>°₁,</th><th>\$ chan</th><th>ge in <p<sup>np2</p<sup></th><th></th></p<>	n 12 <sup>&gt;</sup>	<b>6</b>	:hange in <₁	°₁,	\$ chan	ge in <p<sup>np2</p<sup>	
3	חקקער	n = -1	n = 1	n = 2	n = -1	n = 1	с = ц	1 1 1	-    2	C       
	OA~A	1002 01					1		=	n = 2
		+0.001	-1.6396	-4.2936	-0.0031	+0.0009	+0.0682	-1.3476	-2.5661	-11 72RO
(	Na La	-0.0617	+0.0894	+0.2488	-0.7068	+0.2557	+0.4160	-0 9936	TO RARA	- 1 E005
n	KBLA	+0.0328	-0.0795	-0.2191	-0.6967	+0.0843	+0.0232	-0.8583	+0.4814	-19 7570
	Total	+0.1472	-0.6751	-2.0886	-0.6131	+0.0926	+0.1460	-0.9574	-1.7561	-11 0490
	K aK B	+0.6328	-1 2846	-1 2524						
	Kala	-0.0066	6630 UT		110.0-	-0.0127	+0.0110	-0.7474	-1.7780	-8.0656
4	KAT			+0.1045	-0.3160	+0.2181	+0.4233	-0.5294	+0.4934	+1.2014
4			-0.1000	-0.3014	-0.2995	-0.0176	-0.1350	-0.4505	-0.1662	-4.2838
	Total	+0.1845	-0.5463	-1.6017	-0.2633	+0.0500	+0.0809	-0.5141	-1.1478	-7.4522
	K aK B	+0.5715	-1.0257	-7 5715	0110	C 10 0				
	KaLa	+0 0057	+0.0410	LO 1122			-0.0042	-0.4991	-1.2739	-6.0991
S	KBLA	+0.0370			-0.14/9	+0.1804	+0.3827	-0.3103	+0.6329	+0.9715
)		2	0.21.0-	1007.0-	-0.1307	-0.0560	-0.1863	-0.2617	-0.3580	-3.9214
	Total	+0.1718	-0.4373	-1.2215	-0.1260	+0.0294	+0.0502	+0.3086	-0.8637	-5.6065
	K aK B	+0.4565	-0.7584	-1.8523	-0.0119	-0 0059	-0.0035			
	Ka La	+0.0074	+0.0421	+0.1153	-0.0132	+0.2018	1012 01		-0.0224	-4.0608
~	KB La	+0.0274	-0.1217	-0.2890	+0.0015	-0.0565	-0.1948	-0.0971	-0.2285	+0.6805
	Total	+0.1395	-0.3253	-0.3560	-0.0069	+1.1252	+0.0294	-0.1292	+1.4414	-3.7434
	KaKB	+0.4116	-0.6690	-1.6325	-0 0114	0.00				
	KaLa	+0.0068	+0.0275	+0 1000			+0.0026	-0.2413	-0.6904	-3.4560
80	KB La	+0.0229	-0.1148	-0.2778		111.01	+0.2877	-0.0527	+0.1478	+0.5806
						0/10.0-	-0.1890	-0.0414	-0.4467	-2.9004
	rotal	9621.0+	-0.2913	-0.7970	+0.0293	+0.0107	+0.0279	-0.0714	-0.5051	-3.2016
Та	ble 3.1	<u>.5</u> The pe	rcentage ch	ange in <p<sup>n1</p<sup>	2 <sup>2</sup> , <p<sup>n<sup>1</sup>&gt; a</p<sup>	nd <p<sup>np<sup>n</sup>2 d</p<sup>	ue to corre	elation for	the (1s <sup>2</sup> 2s	) <sup>2</sup> S state

for the Li-like ions.



Figure 3.1.1 The HF function  $f(P_{12})$  for the  $(1s^22s)^2S$  state for Li, Be<sup>+</sup>, B<sup>2+</sup>, c<sup>3+</sup>, N<sup>4+</sup> and o<sup>5+</sup> plotted against the scaled distance  $z^{-1}p_{12}$  (in atomic units). (A) The KAK $\beta$ -shells, (B) the KaLa-shells, (C) the K $\beta$ La-shells, and (D) the total distribution when normalized to unity.





Figure 3.1.2 The Coulomb shifts  $\Delta f(p_{12})$  vs  $Z^{-1}p_{12}$  for the  $(1s^22s)^2S$  state derived for Li, Be<sup>+</sup>, B<sup>2+</sup>, N<sup>4+</sup> and 0<sup>5+</sup>. (A) The KaKβ-shells, (B) the KaLa-shells, (C) the KβLa-shells, and (D) the total Coulomb shift for each Z obtained here by taking  $1/3 \sum_{i \le j}^{3} \Delta f_{ij}(p_{12})$ .

All curves are ordered at  $2^{-1}p_{12}=0.5$  such that, as Z increases the  $\Delta f(p_{12})$  value decreases.



Figure 3.1.3 A comparisons of the Coulomb shifts,  $\Delta f(p_{12})$  vs.  $Z^{-1}p_{12}$ , for the KaK $\beta$ -shell for Li(<sup>2</sup>S), Li<sup>+</sup>(<sup>1</sup>S), Be<sup>+</sup>(<sup>2</sup>S), Be<sup>2+</sup>(<sup>1</sup>S) and Be(<sup>1</sup>S). The results for Li<sup>+</sup>(<sup>1</sup>S) and Be<sup>2+</sup>(<sup>1</sup>S) are taken from Reed<sup>(77)</sup> and the Be(<sup>1</sup>S) result is taken from Banyard and Mobbs<sup>(65)</sup>.



and  $K\beta L\alpha$  (----) shells in the  $(1s^2 2s)^2 s$  state of (A) Li, (B) Be<sup>+</sup> and (C) N<sup>4+</sup>. The Sum Total (----) of these contributions is given by KaKB + KaLa + KetaLa. The  $\Delta f(p_{1,2})$ -scale for Sum Total Coulomb shift is the same as that for the KaKB-shell which is shown on the **Figure 3.1.4** A comparison of the Coulomb shifts vs.  $z^{-1}p_{12}$  for the KaKB(---), KaLa(---) left of each diagram. The **Af(p<sub>12</sub>) scales for Li, Be<sup>+</sup> and N<sup>4+</sup> are marked in increments of 1 x** Q, 5 **x** Q and 2 **x** Q, respectively, where Q is given on the top of each ordinate. the

Figure 3.1.5

(see over)

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Figure 3.1.5 The HF surface  $g(p_{12}, p_1)$  vs.  $(p_{12}, p_1)$  for the Li, Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^2 2s)^2 s$  state. (A) The KuKB-shells (top row), (B) the  $K\alpha L\alpha$ -shells (middle row) and (C) the K $\beta$ L $\alpha$ -shells (bottom row). Note that each column corresponds

to a given atom.







Figure 3.1.6

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(see over)
The partial Coulomb shift  $\Delta g(p_{12}, p_1)$  vs.  $(P_{12},P_1)$  for the Li, Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^22s)^2s$  state. (A) The KaKB-shells (top row), (B) the KaLa-shells (middle row) and (C) the KpL $\alpha\text{-shells}$  (bottom row ). Note that each column corresponds to a given atom. Figure 3.1.6





Bet



Figure 3.1.7 (see over)

densities  $D(p_1, p_2)$  in the  $(1s^2 2s)^2 s$  state for Li, Be<sup>+</sup> and **Figure 3.1.7 A comparison of the HF two-particle radial**  $N^{4+}$ . (A) The KaKB-shells (top row), (B) the KaLa-shells (middle row) and (C) the K $\beta$ L $\alpha$ -shells (bottom row). Note that each column corresponds to a given atom.





(see over)

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Li, Be<sup>+</sup> and N<sup>4+</sup>. (A) The KaKβ-shells (top row), (B) the Figure 3.1.8 A comparison of the change in  $D(P_1, P_2)$ , relative to the HF distribution, for the  $(1s^22s)^2s$  state for  $K\alpha L\alpha\text{-shells}$  (middle row) and (C) the K\beta L\alpha\text{-shells} (bottom row). Note that each column corresponds to a given atom.





Bet









<u>Figure 3.1.10</u> Varition of radial and angular correlation coefficients plotted against  $z^{-1}$ , for the KaKβ-shell in the  $(1s^22s)^2S$  state.

Tables and Figures for the <sup>2</sup>P-states

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			d/2⊈, 1 <sup>4</sup> 2	<sup>n</sup> P <sup>n</sup> 2			~	p12>				∆P12
2	SHELL	n = 2	n = 1	0 = u	" 2	- 1	# L	-	1	2		]
		CORR	CORR	CORR	HF	CORR	HF	CORR	HF	CORR	НF	aaco
	Ka KB	+0.0076	+0,0369	+0 3140	0 4750	0 4373	3 2025	2222				CUMN
	KaLa	-0.1769	-0.0617	-0.0472	C 225.0			3.2322	14.1920	13.5977	1.8485	1.7750
<u>m</u>	Κβ Lα	-0.0062	-0.0039	-0.0038	0.6315	0.6292	2.3028	2.3330	2016./	7.5223	1.4397	1.4411
	Total	-0.0585	-0.0096	+0.0877	0 5496	0 5489	7053 0				<b>4</b> /0 <b>4</b> ,1	1.4600
						60 <b>6</b> 0.0	0600.2	2.0240	9.0/.6	9.5260	1.6568	1.6241
	KaKB	+0.0027	+0.0267	+0.4375	0.3095	0.3101	4.4758	4.4282	25.8578	25 1307	2518 C	0006 C
•	Kala	-0.1051	-0.1219	-0.2773	0.3920	0.3918	3.3543	3.3526	14.7466	14 7218	0015.7	1 0650
4	KB La	-0.0031	-0.0045	-0.0090	0.4398	0.4373	3.2420	3.2520	14.2063	14.2727	1.9225	1 9228
	Total	-0.0351	-0.0332	+0.0504	0.3804	0.3797	3.6907	3.6776	18.2702	18.0418	2.1562	2.1253
	KaKB	+0.0013	+0.0208	+0.5583	0.2424	0 2428	5 7211	5 6703	0007 07			
	Ka La	-0.0649	-0.1535	-0.6855	2222.0				42.4409	41.4811	3.1246	3.0543
S	KB La	-0.0015	-0.0038	-0.0123	0.3358	0.3338	4.2136	4 2278	2162.02 23 9080	8061.62	2.4025	2.3959
	Total	-0.0217	-0.0455	-0.0465	0.2905	0 2898	CC87 4	A 7605	30 5464			2.4003
				22.2	001310	0.2020	770/.2	CK0/.#	30.2464	30.2329	2.7707	2.7359
	KαKβ	+0.0007	+0.0171	+0.6797	0.1993	0.1996	6.9468	6.8957	62.5220	61 2894	3 7768	3 7055
•	Kara	-0.0436	-0.1723	-1.2611	0.2343	0.2340	5.4698	5.4683	38.3635	38 3001	001100	0000
ø	KBLa	-0.0008	-0.0031	-0.0147	0.2716	0.2700	5.1799	5.1963	35.8642	36.0286	3.0055	3.0045
	Total	-0.0145	-0.0528	-0.1987	0.2350	0.2345	5.8655	5.8534	45.5832	45.2060	3.3436	3.081
	KaKB	+0.0004	+0.0145	+0.8018	0.1700	0.1701	8.0488	8.0075	81.9388	BO RA69	4 1420	0000
٢	Kala	-0.0311	-0.1839	-1.9933	0.1953	0.1951	6.4815	6.4802	52.6055	52.5384	3.2551	3.2474
•		cono.o-	-0.0026	-0.0167	0.2283	0.2271	6.1018	6.1189	48.6069	48.8842	3.3845	3.3829
	Total	-0.0104	-0.0574	-0.4027	0.1979	0.1975	6.8774	6.8688	61.0504	60.7565	3.7084	3.6845
Ta	ble 3.	1.6 Some	two-par	ticle ex	pectatio	n prope	rties f	or the (	1s <sup>2</sup> 2p) <sup>2</sup> p	state for	the ind.	lauhiv
		shell	ls and th	e normali	zed Tota	l values	for the	Li-like	ions. T	hese resu	lts are d	lerived.
		by ut	sing Weis:	s <sup>(26)</sup> cI 4	and Veis	5 <sup>(26)</sup> HF	wavefun	ctions.				

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				d ~	~ ~				Δp.		Δ1/	- d
Z SHELL	" 2	-2	н Д		u	-	" 2	2				
	HF	CORR	HF	CORR	ΗF	CORR	HF	CORR	HF	CORR	HF	CORR
ΚαΚβ Καία 3 Κβία	0.7642 4.7340	0.7638 4.6656 4.6617	0.6574 1.6363	0.6573 1.628 <b>4</b> 1.6272	2.2456 1.3605	2.2463 1.3603 1.3626	7.2237 3.7529	7.2323 3.7518 3.7629	1.477	1.479	0.576 1.434	0.576
Total	3.4108	3.3637	1.3100	1.3043	1.6555	1.6564	4.9099	4.9157	1.473	1.474	1.302	1.289
ΚαΚβ ΚαΙα 4 ΚβΙα	0.3988 1.2677	0.3991 1.2742 1.2701	0.4756 0.8846	0.4756 0.8877 0.8859	3.0880 2.0252	3.0884 2.0200 2.0273	13.5526 7.3539	13.5604 7.3538 7.3798	2.004 1.803	2.006 1.809	0.415 0.697	0.416 0.697 0.697
Total	0.9781	0.9811	0.7483	0.7498	2.3795	2.3786	9.4202	9.4313	1.939	1.943	0.647	0.647
ΚαΚβ Καια 5 Κβια	0.2437 0.5979	0.2440 0.5970 0.5971	0.3723 0.6184	0.3723 0.6195 0.6179	3.9319 2.6845	3.9321 2.6793 2.6895	21.8704 12.2181	21.8773 12.1756 12.2665	2.532 2.239	2.533 2.235 2.243	0.324 0.464	0.325 0.465 0.464
Total	0.4798	0.4803	0.5364	0.5366	3.1003	3.1003	15.4356	15.4398	2.413	2.414	0.438	0.439
KaK B KaLa 6 KBLa	0.1640 0.3519	0.1642 0.3519 0.3503	0.3056 0.4786	0.3057 0.4787 0.4775	4.7773 3.3408	4.7773 3.3361 3.3477	32.1849 18.3378	32.1911 18.2812 18.4070	3.060 2.679	3.061 2.674 2.683	0.266	0.266 0.350 0.350
Total	0.2893	0.2888	0.4209	0.4206	3.8196	3.8204	22.9535	22.9598	2.892	2.892	0.335	0.335
ΚαΚβ Καία 7 Κβία	0.1177 0.2331	0.1179 0.2327 0.2316	0.2592 0.3913	0.2593 0.3912 0.3903	5.6236 3.9953	5.6235 3.9908 4.0031	44.4978 25.7099	44.5027 25.6393 25.7955	3.588 3.122	3.589 3.117 3.126	0.225 0.283	0.225 0.282 0.282
Total	0.1946	0.1941	0.3473	0.3469	4.5381	4.5391	31.9725	31.9792	3.373	3.373	0.272	0.272
Table 3.	1.7 Ext for	pectation r the ir	values dividual	<pre><pre><pre><pre><pre><pre><pre><pre></pre></pre></pre></pre></pre></pre></pre></pre>	the sta	ndard der	riations	$\Delta p_1$ and $\Delta$	1/p for	the (1	<sup>s<sup>2</sup>2p)<sup>2</sup>p</sup>	state
	re.	sults are	derived t	or using	Weiss <sup>(</sup> 26	CI and	Weiss <sup>(26</sup>	al values ) HF wave:	for the	e Li-li. 1s.	ke ions	. The

					<pre>     b     1     1 </pre>	p <sup>n</sup> >				<b></b>
27	SHELL	= u	-2	" "	-	= u	-	" "	- 2	1
		HF	CORR	HF	CORR	HF	CORR	HF	CORR	
<b>m</b>	Ka Kp Ka La Kb La	0.5840 6.6517 *	0.5381 6.5100 6.4901	0.4322 1.7193	0.4226 1.7069 1.7037	5.0429 1.0675	4.9064 1.0661 1.0706	52.1825 2.0378	45.8875 2.0058 2.0371	1
	Total	4.6291	4.5127	1.2903	1.2777	2.3926	2.3477	18.7527	16.6434	
4	ΚαΚβ Κα Lα Κβ Lα	0.1591 0.8521	0.1505 0.8490 0.8418	0.2262 0.6153	0.2227 0.6171 0.6141	9.5358 2.9722	9.3522 2.9408 2.9637	183.6736 15.6572	167.8636 15.1954 15.5214	
	Total	0.6211	0.6137	0.4856	0.4846	5.1601	5.0856	71.6626	66.1935	
ى د	KαKβ KuLa KβLa Total	0.0541 0.2320 0.1745	0.0569 0.2307 0.3219 0.1720	0.1386 0.3219 	0.1370 0.3221 0.3202 0.2597	15.4599 5.6507 8.9204	15.2291 5.6111 5.6541 8.8315	478.3151 56.1140 169.8477	446.3394 54.8876 55.9349 185.7206	1
و	KαKβ KαLα KβLα Total	0.0269 0.0885 0.0680	0.0260 0.0878 0.0868 0.0868	0.0934 0.1991 0.1639	0.0926 0.1989 0.1977 0.1631	22.8225 9.0972 13.6723	22.5444 9.0535 9.1150 13.5709	1035.8644 144.5313 441.6423	979.2786 144.0253 144.3289 415.2102	
7	KaK A KaLa KBLa Total	0.0139 0.0410 0.0320	0.0135 0.0407 0.0402 0.0315	0.0672 0.1357 0.1128	0.0667 0.1354 0.1347 0.1347 0.1123	31.6251 13.3114 19.4160	31.2992 13.2601 13.3386 19.2993	1980.0562 308.0286 865.3711	1888.5932 303.3989 307.6244 833.2055	· · · · · · · · · · · · · · · · · · ·
Tal	2 <mark>1e 3.1.8</mark>	Expectat the no:	tion values rmalized T	$\langle p_1^n p_2^n \rangle f_i$	or the (1s es for the	<sup>2</sup> 2p) <sup>2</sup> p sta Li-like i	te for the . .ons. The .	individual results are	shells and derived by	<b>_</b>

using Weiss<sup>(26)</sup> CI and Weiss<sup>(26)</sup> HF wavefunctions.

a distribution correlation	cicle momentum è to electron	the interpart stributed due	etcentage ut las been re-di	(P4,) which h	function f <sub>ut</sub>		
Li-like ions	shells in the	l electronic s	le individua]	tate for th	Also listed		
ents r for the	cion coefficie	yular correlat	adial and and	Δτ in the r	The change	le 3.1.9	Tab
0.2861	+0.00293	-0.00077	+0.00795	-0.00463	-0.01113	Total	
0.2945	-0.00262	-0.00212	-0.00065	-0.00363	-0.00293	NBLA	-
0.1376	-0.00306	-0.00149	-0.00111	-0.00224	-0.00252	Ka la	٢
0.4853	+0.01446	+0.00360	+0.01802	-0.01082	-0.02523	KaKB	
0.3450	+0.00338	-0.00088	+0.00935	-0.00540	-0.01284	Total	
0.3318	-0.00314	-0.00237	-0.00080	-0.00419	-0.00310	KB La	9
0.6053	+0.01706	+0.00427	+0.02111	-0.01283	-0.02974	ΚαΚβ Κα La	
0.3910	+0.00427	-0.00083	+0.01145	-0.00633	-0.01516	Total	
0.3519	-0.00381	-0.00256	-0.00100	-0.00511	-0.00329	KB La	ŝ
0.7286	+0.02081	+0.00525 -0.00135	+0.02552 -0.00149	-0.01573 -0.00 <b>4</b> 33	-0.03619 -0.00322	ΚαΚβ Κα La	1
0.4202	+0.00569	-0.00088	+0.01475	-0.00720	-0.01799	Total	
0.3188	-0.00451	-0.00246	-0.00121	-0.00707	-0.00324	Kβ Lα	4
0.9007	+0.02672	+0.00687	+0.03227	-0.02020 -0.00698	-0.04621 -0.00086	ΚαΚβ Κα La	
0.4827	+0.00935	-0.00066	+0.02068	-0.00340	-0.02175	Total	
0.1923	-0.00393	-0.00133	-0.00102	-0.00284	-0.00033	KBLO	n
1.2363 0 1002	-0.00492	-0.00176	-0.00141	-0.00315	-0.00058	KaLa	¢
					19630 U-	Kr KB	
۲	Δτγ.	۵۳ ۲.	۵۲ <sub>۲</sub>	Δτ1/P	ÅT	SHELL	2

-0.05688 -0.11676 -0.14932 -0.16848 -0.18086	-0.03615 -0.08093 -0.10689 -0.12398 -0.13212	-0.01116 -0.03613 -0.05481 -0.06760 -0.07663	
-0.18086	-0.13212	-0.07663	7
-0.16848	-0.12398	-0.06760	Q
-0.14932	-0.10689	-0.05481	ŝ
-0.11676	-0.08093	-0.03613	4
-0.05688	-0.03615	-0.01116	e
۰ <sup>۲</sup>	۰ <mark>۴</mark>	۲ ۲	2

For the	results.
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in th	lells,
shell	Kβ Lα-si
Ka La -	and
the	Ka Kβ -

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		**	change in <	p12>	0 00	:hange in <∣	p1,	U 90	:hange in <p< th=""><th>npn&gt;,1p2</th></p<>	npn>,1p2
2	SHELL	n = 1	н ц	n = 2	n = -1		n = 2	ר וו ר	۲ ۱ ۲	
	KaKB	+0.2921	-1.5336	-4 1873	-0.0106			-	11	7 = U
	ΚαΓα	-0.1659	+0.0746	+0.1620	-0.4841	+0.0304 -0 0143	+0.1179	-0.2214	-2.7069	-12.0635
m	KβLα	-0.3674	+0.2236	+0.4185	-0.5567	+0.1510	+0.2662	CU2/.U-	-0.1282	- 1.5734
	Total	-0.1248	-0.5487	-1.8916	-0.4366	+0.0512	+0.1179	-0.9713	-1.8766	-11 2470
	K olk B	+0.2168	-1.0619	-2.8118	+0.0055	+0 0120	40 0573			
	Kala	-0.0577	-0.0501	-0.1682	+0.3519	-0.2588		1250.1-	-1.9252	- 8.6077
4	KB La	-0.5775	+0.3103	+0.4677	+0.1449	+0.1004	+0.3511	-0.1981	-1.0555 -0 2853	- 2.9491
	Total	-0.1861	-0.3536	-1.2506	+0.1968	-0.0397	+0.1185	-0-1983	1 4430	- 0.00/3
	0 ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~									0100.1 -
	vu∧p K~1~		-0.88/8	-2.3834	+0.0180	+0.0046	+0.0316	-1.1597	-1.4927	- 6 6851
Ľ	VOT	-0.1030	-0.03/4	-0.1837	+0.1695	-0.1944	-0.3484	+0.0652	-0.7002	- 2 1856
ר 	Der du	c020.0-	+0.3380	+0.4960	-0.0786	+0.1852	+0.3960	-0.5170	+0.0603	- 0.3191
	Total	-0.2224	-0.2669	-1.0264	+0.0393	-0.0007	+0.0275	-0.3912	-0.9975	- 5.6526
	ΚαΚβ	+0.1566	-0.7352	-1.9715	+0.0275	+0 0011	+0 0104			
	KaLa	-0.1153	-0.0263	-0.1653	+0.0217	-0.1396		4010-0-	-1.2186	- 5.4627
<u> </u>	KBLa	-0.5807	+0.3164	+0.4584	-0.2230	+0.2085	+0.3774	-0.6926	-0.4809 +0 1950	-15.5733
	Total	-0.2178	-0.2053	-0.8275	-0.0696	+0.0205	+0.0274	-0.5010	-0.7414	- 5.9850
	K ork B	+0.0977	-0.5127	-1.3326	+0.0401	-0 0015	+0 0100			
	KaLa	-0.0978	-0.0202	-0.1275	-0.0340	-0 1133	2010.01		-1.0306	- 4.6192
~	KB La	-0.5107	+0.2791	+0.5704	-0.2607	+0.1946	+0.3329	-0.1022	-0.3855 -0.40	- 1.5030
	Total	-0.2006	-0.1239	-0.4814	-0.1017	+0,0232	+0 0207			
							10-20-20-	0767.0	-0.6011	- 3.7170
Tat	<b>le 3.1</b>	.11 The	percentage	change in	<p<sup>n2&gt;, <p<sup>n2&gt;</p<sup></p<sup>	and $\langle p_1^n p_2^n$	> due to cc	rrelation	for the (1s	2 <sub>20</sub> , 2 <sub>0</sub>

state for the Li-like ions.

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Figure 3.1.11 The Hf function  $f(p_{12})$  for the  $(1s^22p)^2p$ state for Li, Be<sup>+</sup>, B<sup>2+</sup>, C<sup>3+</sup>, N<sup>4+</sup> and O<sup>5+</sup> plotted against the scaled distance  $2^{-1}p_{12}$  (in atomic units). (A) The KaKβshells, (B) the KaLa-shells, (C) the KβLa-shells, and (D) the total distribution when normalized to unity.





<u>Figure 3.1.12</u> The Coulomb shifts  $\Delta f(p_{12})$  vs  $Z^{-1}p_{12}$  for the  $(1s^22p)^2P$  state derived for Li, Be<sup>+</sup>, B<sup>2+</sup>, C<sup>3+</sup> and N<sup>4+</sup>. (A) The KaKβ-shells, (B) the KaLa-shells, (C) the KβLa-shells, and (D) the total Coulomb shifts for each Z obtained here by taking  $1/3 \int_{i < j}^{3} \Delta f_{ij}(p_{12})$ .

When  $\Delta f(p_{12})$  is positive the curves are ordered from left to right as Z increases in value.



Figure 3.1.13 The  $\Delta f(p_{12})$  comparisons for the KaKβ-shell in  $Li(^{2}P)$ ,  $Li(^{2}S)$  and  $Li^{+}(^{1}S)$ , and also for  $Be^{+}(^{2}P)$ ,  $Be^{+}(^{2}S)$  and  $Be^{2+}(^{1}S)$ . The results for  $Li^{+}(^{1}S)$ ,  $Be^{2+}(^{1}S)$  are taken from Reed<sup>(77)</sup>.



**Figure 3.1.14** A comparison of the Coulomb shifts vs.  $z^{-1}p_{12}$  for the KaK $\beta(---)$ , KaLa(----) and K $\beta$ La(----) shells in the  $(1s^22p)^2p$  state of (A) Li, (B) Be<sup>+</sup> and (C) N<sup>4+</sup>. The Sum Total (----) of these contributions is given by  $K\alpha K\beta + K\alpha L\alpha + K\beta L\alpha$ . The  $\Delta f(p_{1,2})$ -scale for the sum total Coulomb shift is the same as that for the KaKB-shell which is shown on the left of each are marked in increment of 2 x Q, 2 x Q and 5 x Q respectively, where Q is given on the top of each ordinate. diagram. The  $\Delta f(p_{12})$ -scales for Li, Be<sup>+</sup> and N<sup>4+</sup>

(see over)

Figure 3.1.15 The HF surface  $g(p_{12}, p_1)$  vs.  $(p_{12}, p_1)$  for the Li, Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^22p)^2p$  state. (A) The KaK $\beta$ -shells (top row), (B) the  $K\alpha L\alpha$ -shells (middle row and (C) the KBLa-shells (bottom row). Note that each column corresponds

to a given atom.







(see over)

Figure 3.1.16 The partial Coulomb shift  $\Delta g(p_{12},p_1)$  vs.  $(P_{12}, P_1)$  for the Li, Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^22p)^2p$  state. (A) and (C) the KBL $\alpha$ -shells (bottom row). Note that each column The  $K_{\alpha}K\beta$ -shells (top row), (B) the KaLa-shells (middle row) corresponds to a given atom.







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(see over)

The HF surface  $g(p_{12}, p_1, \theta_1)$  for the measured relative to the symmetry axis of the positive lobe of the 2p orbital. Note that each row corresponds to a given Surfaces are shown for  $\theta_1 = 0$ , 30, 60 and 90, where  $\theta_1$  is atom with each surface having scales identical with that for  $K\alpha L\alpha$ -shell for Li, Be<sup>+</sup> and N<sup>4+</sup> in the (1s<sup>2</sup>2p)<sup>2</sup>p state. Figure 3.1.17

θ<sub>1</sub> = 0.



(see over)

The HF surface g(p<sub>12</sub>, p<sub>1</sub>, 8<sub>1</sub>) for the Surfaces are shown for  $\theta_1 = 0^{\circ}, 30^{\circ}, 60^{\circ}$  and  $90^{\circ}$ , where  $\theta_1$  is measured relative to the symmetry axis of the positive lobe KpLa-shell for Li, Be<sup>+</sup> and  $N^{4+}$  in the  $(1s^22p)^2p$  state. of the 2p orbital. Note that each row corresponds to a given atom with each surface having scales identical with that for Figure 3.1.18

 $\theta_1=0^{\bullet}.$ 



(see over)

Figure 3.1.12 The partial Coulomb shift  $\Delta g(p_{12}, p_1, \theta_1)$  for and  $90^{\circ}$ , where  $\theta_{1}$  is measured relative to the symmetry axis the KaLa-shell for Li, Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^22p)^2p$  state. of the positive lobe of the 2p orbital. Note that each row corresponds to a given atom with each surface having scales The  $\Delta g(p_{12}, p_{1}, 8_{1})$  surfaces are shown for  $8_{1} = 0^{\circ}$ , 30°, 60° identical with that for  $\theta_1 = 0^{\circ}$ .


Figure 3.1.20

(see over)

of the positive lobe of the 2p orbital. Note that each row and 90°, where  $\theta_1$  is measured relative to the symmetry axis Figure 3.1.20 The partial Coulomb shift  $\Delta g(p_{12}, p_1, \theta_1)$  for the KBLa-shell for Li, Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^22p)^2p$  state. corresponds to a given atom with each surface having scales The  $\Delta g(P_{12}, P_1, \theta_1)$  surfaces are shown for  $\theta_1 = 0$ , 30°, 60° identical with that for  $\theta_1 = 0^{\circ}$ .



Figure 3.1.21

(see over)

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densities  $D(p_1, p_2)$  for Li, Be<sup>+</sup> and N<sup>4+</sup> in the  $(1s^2 2p)^2 p$ state. (A) The KaKB-shells (top row), (B) the KaLa-shells (middle row) and (C) the K $\beta$ L $\alpha$ -shells (bottom row). Note that Figure 3.1.21 A comparison of the HF two-particle radial each column corresponds to a given atom.







Figure 3.1.22 (see over)

Li, Be<sup>+</sup> and  $N^{4+}$ . (A) The KaKβ-shells (top row), (B) the **Figure 3.1.22** A comparison of the change in  $D(p_1, p_2)$ relative to the HF distribution, for the  $(1s^22p)^2p$  state for KaLa-shells (middle row) and (C) the KBLa-shells (bottom row). Note that each column corresponds to a given atom.



Be⁺



The HF radial distribution function  $D(p_1)$  in the  $(1s^2 2p)^2 p$  state for  $K\alpha K\beta$ and KaLa = K  $\beta$ La. (A) Li, (B) Be<sup>+</sup>, and (C) N<sup>4+</sup>. Figure 3.1.23



<u>Figure 3.1.24</u> Variation of radial and angular correlation coefficients plotted against  $z^{-1}$ , for the KaKβ-shell in the  $(1s^22p)^2P$  state.

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PART FOUR

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APPENDICES

## APPENDIX A.1

# EVALUATION OF THE SECOND-ORDER REDUCED DENSITY MATRIX FOR THE HF AND CORRELATED ELECTRONIC WAVEFUNCTIONS IN POSITION SPACE FOR THE <sup>2</sup>S- AND <sup>2</sup>P-STATES

Lowdin<sup>(55)</sup> has shown that the reduced density matrices provide a valuable tool for analysing the properties of a wavefunction. The second-order density matrix, expressed in terms of a normalized wavefunction, will be useful in evaluating the Coulomb hole,  $\Delta f(r_{12})$ , for the subsequent discussion of correlation properties.

In the independent-particle model, the wavefunction for a system of N electrons can be expressed as a single Slater determinant, thus

$$\bullet_{HF}(1,2,\ldots,N) = \int (1/N!) \det |\bullet_1(1) \bullet_2(2) \ldots \bullet_N(N)| \qquad A.1.1$$

where  $\bullet$  is an orthonormal spin-orbital and is a function of space and spin coordinates. It is easy to show that single determinant can be written as the antisymmetrized product of all occupied HF spin-orbitals

$$\Phi_{\rm HF}(1,2,\ldots,N) = A\Pi(1,2,\ldots,N) \qquad A.1.2$$

where

$$\pi(1,2,\ldots,N) = \phi_1(1)\phi_2(2)\ldots\phi_N(N) , \qquad A.1.3$$

and  $A^{+}$  is the N-electron antisymmetrizer operator, given by

$$A = \int (1/N!) \Sigma (-)^{P} P$$
, A.1.4  
all p

and P is any permutation of the elctrons, and  $(-)^{P}$  has a value of +1 for an even permutation and -1 for an odd permutation. The factor  $\sqrt{(1/N!)}$  is introduced to ensure that the wavefunction is normalized, i.e.  $\langle \bullet_{HF} | \bullet_{HF} \rangle = 1$  where the notation  $\langle | \rangle$  refers to integration over all the coordinates. Expanding equation (A.1.2), we get

$$\Phi_{HF}(1,2,...,N) = \sum_{i \leq 1}^{N} A_{ij}^{mn} (-)^{P} A_{ij}^{T} A.1.5$$

where

$$\mathbf{A}_{ij}^{\mathbf{mn}} = \mathbf{*}_{i}(\mathbf{m})\mathbf{*}_{j}(\mathbf{n}) - \mathbf{*}_{j}(\mathbf{m})\mathbf{*}_{i}(\mathbf{n}) \qquad \mathbf{A}.1.6$$

and  $\Pi_{ij}$  represents the product of all occupied HF spinorbitals except  $\phi_i(m)$  and  $\phi_j(n)$ ; i and j represent spinorbital labels and m and n refer to electron labels.

For any N-electron atomic system, the two-particle density is defined (67) as

$$\Gamma(\underline{x}_{\underline{m}}\underline{x}_{\underline{n}}|\underline{x}_{\underline{m}}\underline{x}_{\underline{n}}') = \binom{N}{2} \int \Phi(\ldots,\underline{x}_{\underline{p}},\ldots) \Phi^{*}(\ldots,\underline{x}_{\underline{p}},\ldots)(\underline{d}\underline{x}_{\underline{p}}) \cdot A \cdot 1 \cdot 7$$

As usual, <u>x</u> represents the combined space and spin

<sup>&</sup>lt;sup>4</sup>A indicates the antisymmetrizer operator unless stated otherwise.

coordinates of electron p, and  $(d\underline{x}_p)$  indicates integrationsummation over all N electrons except m and n. The factor  $\binom{N}{2}$  ensures that the second-order density matrix  $\Gamma(\underline{x}_m\underline{x}_n|\underline{x}_m'\underline{x}_n')$  is normalized to the number of electron pairs within the system; see, for example, McWeeny and Sutcliffe<sup>(67)</sup>.

Substituting equation (A.1.5) into (A.1.7) yields

$$\Gamma_{HF}(\underline{x}_{m},\underline{x}_{n}) = \binom{N}{2} \int \left\{ \begin{array}{c} \sum_{i < j} A_{ij}^{mn} (-)^{P} A_{ij} \right\} \\ \left\{ \begin{array}{c} \sum_{k < 1} A_{kl}^{mn} (-)^{P} A_{kl} \right\}^{*} (d\underline{x}_{p}) \\ k < 1 \end{array} \right\}$$

The integration in equation (A.1.8) gives zero unless i=k and j=1, therefore

$$\Gamma_{HF}(\underline{x}_{m},\underline{x}_{n}) = \binom{N}{2} \int \left( \sum_{i < j}^{n} A_{ij}^{mn} A_{ij}^{mn*} \int A_{ij}^{mn*} (d\underline{x}_{p}) \right) A_{i,1}$$

$$\Gamma_{HF}(\underline{x}_{m},\underline{x}_{n}) = \binom{N}{2} (N-2)!/N! \sum_{\substack{i \leq j \\ i \leq j}} mn A^{mn*}_{ij} A.1.10$$

where

$$\sum_{\substack{i < j}{}}^{N} A \Pi_{ij} A \Pi_{ij} (d_{\underline{X}_p}) = (N-2)!/N!$$
A.1.11

Since  $\binom{N}{2}(N-2)!/N! = 1/2$ , equation (A.1.10) yields

$$\Gamma_{HF}(\underline{x}_{m},\underline{x}_{n}) = 1/2 \sum_{\substack{i < j}}^{N} A_{ij}^{mn} A_{ij}^{mn*} A.1.12$$

The density for each pair (i,j) is normalized to unity.

To enable us to examine correlation effects within different shells for a given system, the correlated description of the two-particle density was formulated in terms of the many electron theory proposed by Sinanoglu.

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This theory allows us to write the correlated wavefunctions as

$$\Psi_{corr}(1,2,\ldots,N) = c[+_{HF}(1,2,\ldots,N) + X(1,2,\ldots,N)]. A.1.13$$

where the leading term  $\bullet_{\rm HF}$  in equation (A.1.13) is chosen to be the restricted HF wavefunction. Since this reference state is a single determinant, it can be expressed as shown above in equation (A.1.5).

The correlation part X in equation (A.1.13) can be expanded as

$$X(1,2,...,N) = \sum_{i=1}^{N} X_{i} + \sum_{i < j}^{N} X_{ij} + \sum_{i < j < k}^{N} X_{ijk} + ... + X_{ijk...N} A.1.14$$

where

$$X_{i} = A\{ \Pi(1, 2, ..., N) f_{i} / \phi_{i} \}$$
 A.1.15

$$X_{ij} = 2!^{-1/2} A\{ \pi(1,2,...,N) U_{ij}/*_i*_j \}$$
 A.1.16

$$x_{ijk} = 3! / 2 A \{ \pi(1, 2, ..., N) U_{ijk} / *_i *_j *_k \} A.1.17$$

$$X_{ijk...N} = N!^{-1/2} A\{ \Pi(1,2,...,N) \\ U_{ijk...N}^{/\phi} i^{\phi} j^{\phi} k^{...\phi} N \} A.1.18$$

The  $\phi_i$  is the ith normalized HF spin-orbital, and  $f_i$  is the corresponding orbital correction function,  $U_{ij}$  is the pair-correction function associated with  $\phi_i$  and  $\phi_j$ , and  $U_{ijk...}^{U_{ijk...N}}$  are higher many-electron correlation terms. In equation (A.1.15-18), we have used the convention

$$f_{i}/ \bullet_{i} = f_{i}(\underline{x}_{i}) / \bullet_{i}(\underline{x}_{i}) , \ U_{ij}/ \bullet_{i} \bullet_{j} = U_{ij}(\underline{x}_{i}\underline{x}_{j}) / \bullet_{i}(\underline{x}_{i}) \bullet_{j}(\underline{x}_{j}) , \text{ etc.}$$

Expressions for correction functions were obtained by the method of successive partial orthogonalization (MSPO) proposed by Sinanoglu<sup>(36)</sup>. The correlation terms U are antisymmetric under an odd number of permutations, i.e.

$$U_{ij}(X_i, X_j) = U_{ij}(i, j) = -U_{ij}(X_j, X_i)$$
, A.1.19

$$\mathbf{U}_{ijk}(\mathbf{x}_{i},\mathbf{x}_{j},\mathbf{x}_{k}) = -\mathbf{U}_{ijk}(\mathbf{x}_{j},\mathbf{x}_{i},\mathbf{x}_{k}) \quad A.1.20$$

The correlation function X(1,2,...N) in equation (A.1.13) is orthogonal to all the occupied spin-orbitals in  $\phi_{HF}$  since the MSPO procedure is based on the following strong orthogonality requirements

where

$$\langle \mathbf{U}_{\mathbf{i}\mathbf{j}}| \mathbf{*}_{\mathbf{l}} \rangle = \langle \mathbf{U}_{\mathbf{i}\mathbf{j}}(\mathbf{x}_{\mathbf{i}},\mathbf{x}_{\mathbf{j}})| \mathbf{*}_{\mathbf{i}}(\mathbf{x}_{\mathbf{i}}) \rangle_{\mathbf{i}}$$

$$= \int \mathbf{U}_{\mathbf{i}\mathbf{j}}^{*}(\mathbf{x}_{\mathbf{i}},\mathbf{x}_{\mathbf{j}}) \mathbf{*}_{\mathbf{i}}(\mathbf{x}_{\mathbf{i}}) d\mathbf{x}_{\mathbf{i}} = 0 \quad . \qquad A.1.22$$

The partitioning of  $\Gamma_{corr}(\underline{x}_{m},\underline{x}_{n})$  into its pair (i,j) components is, of necessity, only approximate and, as discussed in earlier work<sup>(28)</sup>, the contributions arising from  $\underline{x}^{*}(1,2,\ldots,N)\underline{x}(1,2,\ldots,N)$  will be omitted. Substituting equation (A.1.7) we get,

$$\Gamma_{\text{corr}}(\underline{x}_{m},\underline{x}_{n}) = \binom{N}{2} c \int \left( \phi_{\text{HF}}(1,2,\ldots,N) \phi_{\text{HF}}^{*}(1,2,\ldots,N) + \phi_{\text{HF}}(1,2,\ldots,N) \right) x^{*}(1,2,\ldots,N) + x(1,2,\ldots,N) + x(1,2,\ldots,N) \phi_{\text{HF}}^{*}(1,2,\ldots,N) + x(1,2,\ldots,N) \phi_{\text{HF}}^{*}(1,2,\ldots,N) + x(1,2,\ldots,N) + x(1,2,\ldots,N)$$

If we expand the correlation part X then, according to the orthogonality conditions in equation (A.1.21), the equation (A.1.23) can be written as

$$\Gamma_{\text{corr}}(\underline{x}_{m}, \underline{x}_{n}) = \binom{N}{2} c \left[ \int \phi_{\text{HF}}(1, 2, \dots, N) \phi_{\text{HF}}^{*}(1, 2, \dots, N) + \int \phi_{\text{HF}}(1, 2, \dots, N) \int_{i=1}^{N} \frac{x_{i}}{i + 1} (d\underline{x}_{p}) + \int \phi_{\text{HF}}(1, 2, \dots, N) \int_{i$$

since

$$\int \Phi_{HF}(1,2,...,N) \left\{ \sum_{i < j < k}^{N} X_{ijk} + ... + X_{ijk...N} \right\}^{*} (d\underline{x}_{p}) = 0$$
A.1.25

and

$$\int \{ \sum_{\substack{i < j < k}}^{N} x_{ijk} + \ldots + x_{ijk} + \ldots + x_{HF}^{*}(1,2,\ldots,N) \quad (dx_p) = 0 \\ A.1.26$$

In the present work we are considering three-electron systems, so it is convenient to set m=1 and n=2, and after integration over all electron coordinates except those associated with electrons 1 and 2, equation (A.1.24) becomes, after some considerable manipulation, as follows,  $\Gamma_{\text{corr}}(\mathbf{X}_{1}, \mathbf{X}_{2}) = 1/2 \prod_{i < j}^{3} [\mathbf{A}_{ij}^{12} \ \mathbf{A}_{ij}^{12*} + \mathbf{A}_{ij}^{12} \ \mathbf{B}_{ij}^{12*} + \mathbf{A}_{ij}^{12} \ \mathbf{D}_{ij}^{12*} \ \mathbf{D}_$ 

$$B_{ij}^{12} = \phi_{i}(\underline{x}_{1})f_{j}(\underline{x}_{2}) - f_{j}(\underline{x}_{1})\phi_{i}(\underline{x}_{2}) , \qquad A.1.28$$

$$D_{ij}^{12} = f_{i}(\underline{x}_{1}) *_{j}(\underline{x}_{2}) - *_{j}(\underline{x}_{1}) f_{i}(\underline{x}_{2}) . \qquad A.1.29$$

Equation (A.1.27) can be rewritten as

$$\Gamma_{corr}(\mathbf{X}_{1},\mathbf{X}_{2}) = \prod_{i$$

Finally, when we substitute the  $U_{ij}$  expression (see equation 1.1.16), the equation (A.1.30) becomes

$$\Gamma_{\rm corr}(\underline{X}_1,\underline{X}_2) = \sum_{i < j}^{3} A_{ij}^{12} \left( \langle \Psi_{\rm corr} | \Pi_{ij} \rangle / \langle \Psi_{\rm corr} | \Pi \rangle - 1/2 A_{ij}^{12} \right) .$$
  
A.1.31

In this analysis,  $\Pi_{ij}$  and  $\Pi$  are defined as before (see page 35), and the integrals in  $\langle \Psi_{corr} | \Pi_{ij} \rangle$  are over all the coordinates occuring in  $\Pi_{ij}$  and thus we obtain a function of  $\underline{x}_1$  and  $\underline{x}_2$  only. The term  $\langle \Psi_{corr} | \Pi \rangle$  is the overlap integral.

## APPENDIX A.2

# CALCULATION OF THE f(r12), q(r12+r1) AND

# q(r<sub>12</sub>,r<sub>1</sub>, θ<sub>1</sub>) FUNCTIONS

For any N-electron system the two-particle density can be defined as  $^{(67)}$ 

$$\Gamma(\underline{\mathbf{x}}_{m},\underline{\mathbf{x}}_{n}) = \binom{N}{2} \int \Psi^{*}(\underline{\mathbf{x}}_{1},\underline{\mathbf{x}}_{2},\ldots,\underline{\mathbf{x}}_{N}) \Psi(\underline{\mathbf{x}}_{1},\underline{\mathbf{x}}_{2},\ldots,\underline{\mathbf{x}}_{N})$$
$$d\underline{\mathbf{x}}_{p},\ldots,d\underline{\mathbf{x}}_{N} \qquad A.2.1$$

where  $\underline{x}_{m}$  and  $\underline{x}_{n}$  are the space spin co-ordinates of any two electrons m and n, and  $d\underline{x}_{p}, \dots d\underline{x}_{N}$  indicates integrationsummation over the combined space and spin co-ordinates of all N-electrons except m and n. The factor  $\binom{N}{2}$  ensures that the  $\Gamma(\underline{x}_{m},\underline{x}_{n})$  is normalized to the number of electron pairs within the system, so that

$$\int \Gamma(\underline{\mathbf{x}}_{m}, \underline{\mathbf{x}}_{n}) d\underline{\mathbf{x}}_{m} d\underline{\mathbf{x}}_{n} = \binom{N}{2} \qquad A.2.2$$

For the three-electron systems, the density for the individual electronic shells is obtained by partitioning  $\Gamma$  into its pair-wise components (i,j), and the resulting expression for  $\Gamma$  can be written as

$$\Gamma(\underline{\mathbf{x}}_{m},\underline{\mathbf{x}}_{n}) = \sum_{i < j}^{3} \Gamma_{ij}(\underline{\mathbf{x}}_{m},\underline{\mathbf{x}}_{n}) \qquad A.2.3$$

The i and j values label the occupied spin-orbitals within the HF description and, hence, taken as a pair, (i,j) references the individual electronic shells. As seen in Chapter 2.2.3 (also see Appendix A.1) the partioning of

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 $\Gamma_{\rm HF}(\underline{x}_{\rm m},\underline{x}_{\rm n})$  is exact whereas, for the correlated two-particle density, the resolution may be achieved only approximately.

The interparticle distribution function associated with the spin orbital pair (i,j) is given by

$$f_{ij}(r_{12}) = \int \Gamma_{ij}(\underline{x}_1, \underline{x}_2) d\underline{x}_1 d\underline{x}_2 / dr_{12}$$
 A.2.4

such that, for any pair (i,j) we have

$$\int_{0}^{\infty} f_{ij}(r_{12}) dr_{12} = 1 , \qquad A.2.5$$

where for convenience we have set m and n to be 1 and 2. After integration over the spin co-ordinate, equation (A.2.4) reduces to

$$f_{ij}(r_{12}) = \int \Gamma_{ij}(r_1, r_2) dr_1 dr_2 / dr_{12}$$
 A.2.6

where  $\Gamma_{ij}(\underline{r}_1,\underline{r}_2)$  is the spin-free second-order density, and  $\underline{r}_1$  represents the space coordinates of electron 1. The element of volume  $d\underline{r}_i$  is defined as

$$d\underline{r}_{i} = r_{i}^{2} \sin\theta_{i} d\theta_{i} d\phi_{i} dr_{i}$$
 A.2.7

The integration in equation (A.2.6) is to be performed over all coordinates except  $r_{12}^{}$  and the integration region in this equation is just that used by Coulson and Neilson<sup>(63)</sup>.

physically,  $f(r_{12})dr_{12}$  can be interpreted as the probability that the distance separating electrons 1 and 2 lies somewhere between  $r_{12}$  and  $r_{12} + dr_{12}$ . In order to

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calculate  $f(r_{12})$  we express equation (A.2.6) in terms of  $r_{1'}$  $r_2$  and  $r_{12}$ ; all angular terms must be integrated out. To reach this stage we start by transforming the density and elemental volume in an appropriate manner by selecting the  $\bar{r}_1$ -direction to be the new polar axis. Transformations of the element volume in equation (A.2.6) may therefore be acheived by rotating the coordinate system through the Euler angles  $\alpha\beta\gamma$ , see Figure A.2.1, whence

$$d\mathbf{r}_2 = r_2^2 dr_2 \sin\theta_{12} d\theta_{12} dX$$
 A.2.8

From the law of cosines

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_{12}$$
 A.2.9

we obtain

$$r_{12}dr_{12} = r_1r_2 \sin\theta_{12} d\theta_{12}$$
 A.2.10

provided that  $r_1$ ,  $r_2$  are kept fixed. The combined volume element therefore becomes

$$dr_{1}dr_{2}/dr_{12} = r_{1}r_{2}r_{12}dr_{1}dr_{2}sin\theta_{1}d\theta_{1}d\phi_{1}dx \quad A.2.11$$

Substituting equation (A.2.11) into (A.2.1) we get

$$f(r_{12}) = r_{12} \int \Gamma(r_1, r_2) r_1 r_2 dr_1 dr_2 \sin\theta_1 d\theta_1 d\phi_1 dx , \quad A.2.12$$

where X denotes an angle of rotation of the plane 012 around 01 and, for a given  $r_{12}^{}$ , the allowed values of  $r_1^{}$  and  $r_2^{}$  are

$$r_{12} - r_1 < r_2 < r_{12} + r_1 \quad (r_1 < r_{12})$$
  
 $r_1 - r_{12} < r_2 < r_{12} + r_1 \quad (r_1 > r_{12}) \quad . \qquad A.2.13$ 

Equation (A.2.12) can be used in general to evaluate  $f(r_{12})$  for spherically symmetric cases and also for non-spherically symmetric examples, as considered in the following Sections I and II, respectively.

# I. The Spherically-Symmetric Case

If the wavefunction  $\Psi$  in the two-particle density  $\Gamma$ involves only  $r_1$ ,  $r_2$  and  $r_{12}$  then we may integrate over angles mentioned in equation (A.2.12) to give

$$f(r_{12}) = 8\pi^2 r_{12} \{J_1 + J_2\}, \qquad A.2.14$$

where

$$J_{1} = \int_{0}^{r} r_{1} dr_{1} \int_{0}^{r} \Gamma(\underline{r}_{1}, \underline{r}_{2}) r_{2} dr_{2} \qquad A.2.15$$

and

$$J_{2} = \int r_{1} dr_{1} \int \frac{\Gamma(r_{1}, r_{2}) r_{2} dr_{2}}{r_{12}} A.2.16$$

The ranges of the two radial integrations  $J_1$  and  $J_2$  are represented by the shaded area shown in Figure A.2.2.

In order to utilise  $f(r_{12})$ , the wavefunction  $\Psi$  in the  $\Gamma(r_1, r_2)$  must be expressed entirely in terms of  $r_1$ ,  $r_2$  and

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 $r_{12}$ : this is easily carried out by applying the spherical harmonic addition theorem<sup>(85)</sup> to equation A.2.14. This theorem states

$$P_{1}(\cos\theta_{12}) = 4\pi/(21+1) \sum_{\mu=-1}^{+1} Y_{1\mu}^{*}(\theta_{1}, \phi_{1})Y_{1\mu}^{}(\theta_{2}, \phi_{2})$$
 A.2.17

where  $\theta_{12}$  is the angle between  $\underline{r}_1$  and  $\underline{r}_2$ . This gives

$$\sum_{\mu=-1}^{+1} Y_{1\mu}^{\star}(\theta_{1}, \phi_{1}) Y_{1\mu}^{\dagger}(\theta_{2}, \phi_{2}) = \sum_{\mu=-1}^{+1} Y_{1\mu}^{\dagger}(\theta_{1}, \phi_{1}) Y_{1\mu}^{\star}(\theta_{2}, \phi_{2})$$
  
=  $(21+1)/4\pi P_{1}^{\dagger}(\cos\theta_{12}) = A.2.18$ 

The phase of the spherical harmonics used by Weiss in the construction of his wavefunction was  $Y_{1\mu}^{*} = Y_{1-\mu}$ . The argument  $\cos\theta_{12}$  of the Legendre function appears in equation (A.2.18) is

$$\cos\theta_{12} = r_1^2 + r_2^2 - r_{12}^2) / 2r_1r_2$$
 A.2.19

Boyd and Coulson<sup>(64)</sup> defined a function  $g(r_{12}, r_1)$  to represent the probability of finding an interelectronic separation  $r_{12}$  when a test electron is located at a distance  $r_1$  from the nucleus. Therefore, the  $g(r_{12}, r_1)$  function may be calculated by performing only the inner integral in equation (A.2.15) and (A.2.16). This relation may be summarised as

$$f(r_{12}) = \int_{0}^{r_{12}} g(r_{12}, r_{1}) dr_{1} + \int_{r_{12}}^{\infty} g(r_{12}, r_{1}) dr_{1}$$
$$= \int_{0}^{\infty} g(r_{12}, r_{1}) dr_{1} \qquad A.2.20$$

The distribution function  $f(r_{12})$  arising from the spherically-symmetric wavefunctions built from  $1^2$  configurations can be obtained from the use of equations (A.2.14-18). However, many interesting systems are not spherically symmetric<sup>(87)</sup>. In the present analysis the  ${}^2$ P-state of Li-like ions is an example of such a system. The expression for  $f(r_{12})$  obtained from equation (A.2.12) will involve integrals of the most general type

$$I = \int Y_{11m1} (\theta_{1}, \phi_{1}) Y_{12m2}^{*} (\theta_{1}, \phi_{1})$$
  
$$Y_{13m3} (\theta_{2}, \phi_{2}) Y_{14m4}^{*} (\theta_{2}, \phi_{2}) \sin \theta_{1} d\theta_{1} d\phi_{1} dX \quad A.2.21$$

Following the procedure of Calais and Lowdin<sup>(88)</sup>, the reduction of equation (A.2.21) to an integral involving functions of  $r_1$ ,  $r_2$  and  $r_{12}$  can be done by expanding the product of each pair of spherical harmonics with the same argument into a sum of spherical harmonics.

According to Rose<sup>(89)</sup>, equation (A.2.21) becomes

$$I = \sum_{i=1}^{1} \sum_{j=1}^{1} \sum_{i=1}^{2} \sum_{j=1}^{1} \sum_{j=1}^{3} \sum_{i=1}^{4} \left\{ L_{1}L_{2}L_{3}L_{4}/(16\pi\pi LL') \right\}^{1/2}$$

$$C(1_{1}1_{2}1;m_{1}-m_{2}m) C(1_{3}1_{4}1';m_{3}-m_{4}m')$$

$$C(1_{1}1_{2}1;000) C(1_{3}1_{4}1';000) K (-)^{m_{2}+m_{4}}, A.2.22$$

where

$$K = \int Y_{lm}(1)Y_{l'm'}(2) \sin\theta_1 d\theta_1 d\phi_1 dX \qquad A.2.23$$

In equation (A.2.22-23),  $L_i = 2l_i + 1$ ,  $m = m_1 - m_2$  and  $m' = m_3 - m_4$ . The type of Clebsch-Gordan coefficient  $C(l_1 l_2 l; m_1 m_2 m)$  used in this work is that defined by Rose<sup>(89)</sup>.

In order to calculate equation (A.2.22), it is necessary to evaluate the angular integral K. Express the spherical harmonic  $\Psi_{1'm'}(\theta_2, \varphi_2)$  in terms of  $\theta_1$ ,  $\varphi_1, \theta_{12}$  and X. This is equivalent to rotating the coordinate system so that the new polar axis coincides with the  $r_1$  direction. The new polar angles are, of course,  $\theta_{12}$  and X. In other words, we rotate the old system by the Euler angles <sup>(90)</sup>. Thereby the function  $\Psi_{1'm'}(\theta_2, \varphi_2)$  is transformed to

$$J_{1'm'}(\theta_{1'}\phi_{2};\theta_{12'}X) = \Sigma D_{m'm}^{1'}(\alpha\beta\gamma) Y_{1'm}(\theta_{12'}X) \qquad A.2.24$$

where  $D_{m',m}^{1'}(\alpha\beta\gamma)$  are the elements of the rotation matrix as given by Rose<sup>(89)</sup>. The function  $J_{1'm'}(\theta_{1'}, \phi_{2}; \theta_{12'}, \chi)$  depends on  $\chi$  only through the function  $e^{im\chi}$  in the spherical harmonic  $Y_{1'm}(\theta_{12'}, \chi)$ . Consequently, we can integrate over  $\chi$ directly, which reduces the sum in equation (A.2.24) to the single term with m=0. Therefore

$$K = 2\pi \int Y_{lm}(1) \theta_1^0(\theta_{12}) D_m^1(\alpha\beta\gamma) \sin\theta_1 d\theta_1 d\phi_1 \quad A.2.25$$

where  $\theta_{1,(\vartheta_{12})}^{O}$  is the normalized associated Legendre polynomial. But since, for m=0

$$D_{m'O}^{l'} = (4\pi / 2l'+1)^{1/2} Y_{l'm'}^{*} (\theta_{l'}\phi_{l})$$
 A.2.26

we see that equation (A.2.23) becomes

$$K = 2\pi (-)^{m'} P_{1} (\cos \theta_{12}) \delta_{11} \delta_{m-m'}$$
 A.2.27

Substituting equation (A.2.27) into equation (A.2.22) we get

$$I = 1/2 \ (-)^{m_{2}+m_{4}} \frac{1}{2} \frac{1}{1} \frac{1}{1} \frac{1}{2} \frac{1}{2} \frac{1}{1} \frac{3}{1} \frac{1}{4} \left[ L_{1} L_{2} L_{3} L_{4} / LL' \right]^{1/2}$$

$$C(1_{1} 1_{2} 1; m_{1} - m_{2} m) \ C(1_{3} 1_{4} 1^{2}; m_{3} - m_{4} m^{2})$$

$$C(1_{1} 1_{2} 1; 000) \ C(1_{3} 1_{4} 1^{2}; 000)$$

$$(-)^{m_{1}} P_{1^{2}} (\cos \theta_{12}) \delta_{11^{2}} \delta_{m-m^{2}} . A.2.28$$

The distribution function  $g(r_{12}, r_1)$  is determined in the same way as for the spherically-symmetric case. However, in order to calculate  $g(r_{12}, r_1)$  as a function of  $\theta_1$ , we follow the general procedure outlined above. In equation (A.2.25), however, we integrate over  $\varphi_1$  only, hence we get the following relation,

$$\int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{\pi} (r_{12}, r_{1}, \theta_{1}) \sin \theta_{1} d\theta_{1} = \int_{0}^{\infty} g(r_{12}, r_{1}) dr_{1}$$
$$= f(r_{12}) \quad A.2.29$$



<u>Figure A.2.1</u> Coordinate system for the determination of  $f(r_{12})$ ,  $g(r_{12}, r_1)$  and  $g(r_{12}, r_1, \theta_1)$ .



Figure A.2.2 The radial integration range in equation (A.2.14) is represented by the shaded area.

#### APPENDIX A.3

#### MOMENTUM REPRESENTATION OF

# SLATER-TYPE ORBITALS

Momentum space electronic wavefunctions can be obtained through the Fourier transformation (80,91) of ordinary position-space wavefunctions. Thus we may write

$$X_{nlm}(\underline{P}) = 1/\sqrt{((2\pi)^3)} \int X_{nlm}(\underline{r}) \exp(-i\underline{P},\underline{r})d\underline{r} \qquad A.3.1$$

where  $X_{nlm}$  is a Slater-type orbital (STO) and is given by

$$X_{nlm}(\underline{r}) = N_{nlm} Y_{lm}(\underline{Q}) R_{nl}(\underline{r}) . \qquad A.3.2$$

In equation (A.3.2),  $N_{nlm}$  is the normalization factor,  $Y_{lm}(Q)$  is the normalized spherical harmonic, and  $R_{nl}(r)$  is the radial part of the function defined as

$$R_{nl}(r) = e^{-\xi r} r^{n-1}$$

In order to transform  $X_{nlm}(r)$ , we first use an alternative expression for  $exp(-i\underline{P}.\underline{r})$ , written as (92),

$$e^{-i\underline{P}\cdot\underline{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-1}^{l} (-i)^{l} j_{l}(pr) Y_{lm}^{*}(\Omega)Y_{lm}(\Omega) , \quad A.3.3$$

where  $\hat{Q} = \hat{\theta}$ ,  $\hat{\phi}$  and represents the angular variables in momentum space and  $j_1(pr)$  is a spherical Bessel function<sup>(93)</sup>.

$$X_{nlm}(\underline{P}) = N_{nlm} \int (2/\pi) \sum_{\substack{i = 0 \ m' = -1}}^{\infty} \sum_{\substack{i = 0 \ m' = -1}}^{1} (-i)^{i'} Y_{l'm'}(\underline{Q})$$

The angular integration gives rise to the delta functions  $\delta_{11}$ ,  $\delta_{mm}$ , which cancel all terms in the summation except when 1 = 1 and m = m. Thus, we obtain

$$X_{nlm}(\underline{P}) = N_{nlm} R_{nl}(\underline{P}) Y_{lm}(\hat{\Omega})$$
, A.3.5

where

$$R_{n1}(p) = \int (2/\pi) (-i)^1 \int_0^{\infty} j_1(pr) R_{n1}(r) r^2 dr$$
 . A.3.6

Equation (A.3.6) can be written as

$$R_{nl}(P) = (-i)^{1} \int_{0}^{\infty} \int (pr) J_{1+1/2}(pr) R_{nl}(r) r^{2} dr$$
, A.3.6

 $J_{1+1/2}(pr)$  is an ordinary Bessel function of order 1 + 1/2and can be written in terms of a spherical Bessel function through the relation

$$J_{1+1/2}(pr) = (2pr/\pi)^{1/2} j_1(pr)$$
 . A.3.7

Substituting equation (A.3.7) into (A.3.5) yields

$$X_{nlm}(\underline{P}) = N_{nlm}(-1)^{l} 1/\sqrt{(p)} Y_{lm} \int_{0}^{\infty} J_{v}(pr) e^{-\epsilon r} r^{n+1/2} dr$$
, A.3.8  
where  $v = 1 + 1/2$ .

$$\int_{0}^{\infty} r^{n+1/2} e^{-\varepsilon r} J_{v}(pr) dr , \qquad A.3.9$$

which we denote by I, is evaluated by making use of the definite integral (93)

$$\int_{0}^{\infty} e^{-\xi t} J_{v}(bt) t^{v} dt = (2b)^{v} \Gamma(v+1/2) / [J_{\pi}(A)^{v+1/2}], \quad A.3.10$$
where  $A = \xi^{2} + b^{2}$ .

Differentiating q times with respect to the quantity  $\xi$  we obtain

$$\int_{0}^{q} e^{-\xi t} J_{v}(bt) t^{v+q} dt$$

$$= (-)^{-q} (2b) v / \sqrt{\pi} \Gamma(v+1/2) \frac{\partial^{q}(1/A^{v+1/2})}{\partial \xi^{q}} A.3.11$$

If we let q = n-1, t=r and b=p, the integral in Equation (A.3.11) becomes equal to the integral I. Thus in atomic units,

$$I = (-)^{1-n} 2^{1} 1! (2p)^{1+1/2} (2/\pi) \frac{\partial^{n-1} (1/A^{1+1})}{\partial \xi^{n-1}} A.3.12$$

and therefore equation (A.3.8) can be expressed as

$$X_{nlm}(\underline{P}) = N(-)^{n}(2pi)^{l} 1! \sqrt{(2/\pi)} \frac{\partial^{n-1}}{\partial \xi^{n-1}} (A)^{-(l+1)} Y_{lm}(\hat{Q}) A.3.13$$

where

$$N = \int [(2\xi)^{2n+1} / (2n)!] .$$

Below, we present the position and momentum representation of the normalization factor  $N_{nlm}$  and the radial part of the various STO's used in this work.

Orbitals	N <sub>nlm</sub>	Position	Momentum
1s	√(4ξ <sup>3</sup> )	e <sup>-Er</sup>	2ξ√(2/π)A <sup>-2</sup>
2s	√(4ξ <sup>5</sup> /3)	re <sup>-Ęr</sup>	$\int (8/\pi) (3\xi^2 - b^2) A^{-3}$
3 <b>s</b>	√(8Ę <sup>7</sup> /45)	r <sup>2</sup> e <sup>-Er</sup>	$\int (2/\pi) 24\xi (\xi^2 - b^2) A^{-4}$
2p	√(4Ę <sup>5</sup> /3)	re <sup>-Er</sup>	-√(2/π)8piξA <sup>-3</sup>
3p	∫(8Ę <sup>7</sup> /45)	r <sup>2</sup> e <sup>-Er</sup>	$\int (2/\pi) 8pi(b^2-5\xi^2)A^{-4}$
3đ	√(8Ę <sup>7</sup> /45)	r <sup>2</sup> e <sup>-Er</sup>	-48€√(2/m)p <sup>2</sup> A <sup>-4</sup>
4d	2ξ <sup>4</sup> /3√(ξ/35)	r <sup>3</sup> e <sup>-Er</sup>	$48p^2 \int (2/\pi) (b^2 - 7\xi^2) A^{-5}$
5đ	2E <sup>5</sup> /45√(2E/7)	r <sup>4</sup> e <sup>-Er</sup>	$p^2 \sqrt{(2/\pi)\xi(3b^2-7\xi^2)A^{-6}}$
4f	2E <sup>4</sup> /3√(E/35)	r <sup>3</sup> e <sup>-Er</sup>	384p <sup>3</sup> iξ√(2/π)A <sup>-5</sup>
5f	2ξ <sup>5</sup> /45√(2ξ/7)	r <sup>4</sup> e <sup>-Er</sup>	$384p^{3}i/(2/\pi)(9\xi^{2}-b^{2})A^{-6}$
5g	2ξ <sup>5</sup> /45√(2ξ/7)	r <sup>4</sup> e <sup>-Er</sup>	3840p <sup>4</sup> ξ√(2/π)A <sup>-6</sup>

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