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First Order Pair Functions for the Beryllium Isoelectronic Sequence

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The first order pair equations have been solved for the four electron sequence Li^- to Ne^{6+}. A variational perturbation procedure is blended with numerical methods to generate a method for computing pair functions which is both accurate and efficient with respect to time of computation. The variation in the pair correlation energies as a function of atomic number is discussed and the asymptotic behaviour of $E^2(l)$ as l^{-4} and l^{-6} for singlet and triplet states respectively is corroborated. An estimate is made for the electron affinity of lithium.

Die Paargleichungen 1. Ordnung wurden für die Reihe der Ionen mit 4 Elektronen von Li^- bis Ne^{6+} gelöst. Ein Variations-Störungsverfahren wird mit numerischen Methoden verknüpft, um eine Methode zur Berechnung von Paarfunktionen zu erhalten, die genau ist und möglichst geringe Rechenzeiten benötigt. Die Variation der Paarkorrelationsenergien als Funktion der Atomnummer wird diskutiert und das asymptotische Verhalten von $E^2(l)$ wie l^{-4} und l^{-6} für Singulet- und Tripletzustände wird bestätigt. Für Lithium wird die Elektronenaffinität abgeschätzt.

Résolution des équations de paires au premier ordre pour la série à 4 électrons: Li^- à Ne^{6+}. Un procédé de perturbation variationnel est lié à des méthodes numériques pour engendrer une méthode de calcul des fonctions de paires simultanément précise et économique. La variation des énergies de corrélation de paires en fonction du nombre atomique est discutée ainsi que le comportement asymptotique de $E^2(l)$ par rapport à l^{-4} et l^{-6} pour les états singlet et triplet respectivement.

Introduction

There have been numerous attempts to obtain atomic wave functions in which correlation of electron motion is permitted. Amongst review articles concerning the problem, those of Nesbet [1], Sinanoğlu [2], Kelly [3], and Silverman and Bridgman [4] are very informative. Unlike one electron functions, compilations of two electron wave functions for atoms have as yet to appear.

An exact solution of the N electron wave equation for an atom may be expressed in the form

$$\psi = \psi_0 + \sum_{ij} \alpha(ij) + \sum_{ijk} \beta(ijk) + \cdots$$

where the leading term is a Slater determinant composed of one electron functions. This is complemented by successive summations which allow for all two electron, three electron, and higher order interactions respectively. The two electron component is defined by

$$\alpha(ij) = \det|\varphi_1(r_1)\,\varphi_2(r_2)\ldots\varphi_{i-1}(r_{i-1})\,\varphi_{j-1}(r_{j-1}) \cdot \varphi_{i+1}(r_{i+1})\,\varphi_{j+1}(r_{j+1})\,\chi(r_i r_j)| \,.$$

In this expression $\chi(r_i r_j)$ is an antisymmetrised pair function whilst normalisation and antisymmetrisation of $\alpha(ij)$ is implied by the symbol det.

Termination of the series at the opening term ψ_0 and invocation of the variation principle, as is well known, leads to the Hartree-Fock equations for the one electron functions $\varphi_k(r_k)$. On truncation at the second term, there is a choice in the manner in which the equations for the two electron functions may be derived.

If ψ_0 is held to be a determinant of Hartree-Fock one electron functions then the two electron functions are given by the equations derived originally by Sinanoğlu [5] though links to an early study of Fock, Veselov, and Petrashen [6] have been traced. Such equations are also known as the Bethe-Goldstone equations. As Nesbet has succinctly written, "An nth order Bethe-Goldstone equation can be defined as the exact solution of an n-particle Schrödinger equation with the wave function constrained to be orthogonal to the remaining $N-n$ orbitals of an N particle Fermi Sea" [1]. When the one electron functions are determined variationally together with the two electron functions then the one electron functions no longer satisfy the Hartree-Fock equations. Rather they comply to the equations developed by Nesbet following the studies of Brueckner [7] and independently by Szasz [8].

Cogent arguments have been presented for the retention of a Hartree-Fock basis. In the Hartree-Fock model as applied to an atom, each electron is regarded as moving in the field of the nucleus and the spherically averaged charge distribution of the remaining electrons. A natural extension of this model is to permit each pair of electrons to interact directly whilst moving in the nuclear field and the averaged charge distribution of the remaining electrons as described by their Hartree-Fock functions.

Often in the calculation of such pair functions, the Hylleraas inequality is used within a variational perturbation approach. Less frequently numerical methods have been employed. In this study, the central theme of which is a four electron atomic sequence, a blend of the two approaches has been attempted to obtain the first order pair functions.

The Pair Equations

The theory of Sinanoğlu has been delineated several times by a variety of authors and does not require repetition. In the particular example of Beryllium, Byron, and Joachain [9] show that commencing from the functional

$$F(\Phi^t) = \langle \Phi^t | H_0 - E_0 | \Phi^t \rangle + 2 \langle \Phi^t | H_1 - E_1 | \Phi_0 \rangle$$

the pair function from which Φ^t is constituted are given as solutions to the equation of type

$$\begin{aligned} &[H^{\mathrm{HF}}(r) + H^{\mathrm{HF}}(r') - \varepsilon_i - \varepsilon_j]\, \chi_{ij}(r, r') \\ &\quad = -[1/|r-r'| - V_i(r) - V_j(r) - V_i(r') - V_j(r') - \varepsilon^1(ij)] \qquad (1) \\ &\quad \cdot \frac{1}{\sqrt{2}} [\varphi_i(r)\, \varphi_j(r') - \varphi_i(r')\, \varphi_j(r)]\,. \end{aligned}$$

The zeroth order function Φ_0 satisfies the Hartree-Fock equation

$$H_0 \Phi_0 = E_0 \Phi_0$$

with

$$E_0 = \sum_i \varepsilon_i$$

ε_i being the one electron orbital energy. The Hartree-Fock coulomb and exchange energies are expressed within $V_i(r)$

$$\begin{aligned} V_i(r) f(r) = & \int \varphi_i(r') \, 1/|r-r'| \, \varphi_i(r') \, dr' \, f(r) \\ & - \int \varphi_i(r') \, 1/|r-r'| \, f(r') \, dr' \, \varphi_i(r) \end{aligned}$$

$E_1 = \sum_{ij} \varepsilon^1(ij)$ is compounded from such coulomb and exchange terms.

A perturbation arises from the difference between the exact electron interaction and that provided by the Hartree-Fock potential. Corrections to the total energy to third order may then be evaluated in the usual manner. For example with the function Φ^t held orthogonal to Φ_0, the second order energy is given by

$$E_2 = \langle \Phi_0 | H_1 | \Phi^t \rangle .$$

Partitioned as a sum of pair energies

$$E_2 = \sum_{ij} \varepsilon^2(ij)$$

where

$$\begin{aligned} \varepsilon^2(ij) = \Big\langle \chi_{ij}(rr') \Big| & 1/|r-r'| - V_i(r) - V_j(r) \\ & - V_i(r') - V_j(r') - \varepsilon^1(ij) \Big| \frac{1}{\sqrt{2}} [\varphi_i(r) \varphi_j(r') \\ & - \varphi_i(r') \varphi_j(r)] \Big\rangle . \end{aligned}$$

Byron and Joachain discuss further the relative merits of various functional forms to represent the trial function. Adoption of a Legendre expansion for $\chi(r_1 r_2)$ in the manner first suggested by Luke, Meyerott, and Clendenin [10] permits the pair Eq. (1) to be uncoupled.

$$\chi^{ij}(r_1 r_2 \cos\theta_{12}) = 1/4\pi \sum_l U_l^{ij}(r_1 r_2)/r_1 r_2 \cdot P_l(\cos\theta_{12}) .$$

The expansion coefficients may be obtained as solutions to the set of equations of type

$$\begin{aligned} \left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \frac{2Y(r_1)}{r_1} + \frac{2Y(r_2)}{r_2} - \frac{l(l+1)}{r_1^2} - \frac{l(l+1)}{r_2^2} - \varepsilon_i - \varepsilon_j \right] U_l(r_1 r_2) \\ = r_1 r_2 G_l(r_1 r_2) . \qquad (2) \end{aligned}$$

In these equations $Y(r_i)$ is a potential function containing the nuclear and Hartree-Fock potentials, whilst $G_l(r_1 r_2)$ consists of terms arising from the expansion of $1/|r-r'|$, together with the use of Hartree-Fock one electron functions to represent $\varphi_k(r_k)$.

Alternatively the coefficients might be expressed in an analytical form, for example a configuration mixing function could be adopted.

$$U^{ij}_{l\pm}(r_1 r_2) = \Sigma C_{lmn}(r_1^m r_2^n + r_1^n r_2^m) \cdot [(\exp(-\alpha/2 \cdot r_1)\exp(-\beta/2 \cdot r_2) \pm \exp(-\beta/2 r_1)\exp(-\alpha/2 \cdot r_2))]$$

in which the sign indicates the symmetry with respect to the space co-ordinates. The advantages of this type of function are marred by the slow convergence of the series. Accuracy in the calculation of the higher partial waves is inhibited. In an early study of the problem Schwartz remarks "For high l values the most important part of this function is concentrated very sharply about the point $r_1 = r_2$ and a direct attack on the associated two dimensional partial differential equations might be the best way to solve for these highly correlated functions" [11].

It is this suggestion which is pursued further here. The $l = 0$ component is determined using the above type of function in which the number of terms included in the expansion is taken to yield the desired accuracy for the pair under consideration. Higher partial waves are determined by direct solution of the associated differential equations. By proceeding in this manner a further difficulty is obviated. "The 120 strip s wave calculation required the solution of 14000 linear equations which took about 1h on the IBM 360/75. The s wave cut off was taken at 24 a.u. which was still not far enough from the nucleus. Clearly it was not practical to resolve the equations with a larger cut off. The functions for $l > 0$ were much less difficult and could be obtained easily in only a few minutes." Such is the comment of Winter and McKoy in seeking a numerical solution of the hydrogenic pair equation for a three electron atom [12]. This viewpoint is corroborated by the present authors' experience with the helium atom. Numerical calculation of the s wave to an accuracy comparable with the higher waves is the major part of a total numerical calculation. In sharp contrast, the s wave for the (1s 1s) pair of beryllium as obtained here required ~12 secs upon a UNIVAC 1108, the total calculation of all higher waves and energies being completed in the order of four minutes.

The use of finite difference methods in obtaining pair functions for helium has been elaborated in a series of papers by McKoy and Winter which are notable for their clarity [13]. Similar techniques are deployed in this study. The kernel of the approach is to transform the partial differential equations (2) into a set of linear equations by means of a difference approximation. A fourth order difference has been adopted.

$$\frac{\partial^2 f}{\partial r^2} \sim \frac{1}{h^2}\left[-\frac{1}{12}f(r-2h) + \frac{4}{3}f(r-h) - \frac{5}{2}f(r) + \frac{4}{3}f(r+h) - \frac{1}{12}f(r+2h)\right].$$

At the boundary a switch to a second difference is effected. The calculations are performed over a range of grid sizes, defined by h, the equations being solved by the method of successive over-relaxation. By use of the Bolton-Scoins relation linking the energy at $h=0$ to the energies evaluated at other choices for h, accurate values for the energy may be obtained [14].

$$E(h)=E(0)+C_2h^2+C_4h^4+C_6h^6+\cdots .$$

The (1*s* 1*s*), (2*s* 2*s*) and (1*s* 2*s*) pairs of the four electron sequence $\mathrm{Li}^-(1s^2\,2s^2)$ to Ne^{6+} $(1s^2\,2s^2)$ now will be discussed in detail against a comparative background provided by earlier studies.

The (1*s* 1*s*) Pair

Collated in Tables 1, 2 and 3 are the pair correlation energies for the four electron sequence. Beryllium is highlighted in the opening tables.

For the (1*s* 1*s*) pair the results are obtained in the manner which has been discussed. A configuration function is employed of the form

$$\psi(r_1r_2)=\sum_i C_i(r_1^m r_2^n+r_1^n r_2^m)\exp(-\alpha r_1)\exp(-\alpha r_2).$$

That functions of this type simulate very well the behaviour of the *s* wave is indicated by a comparison of the analytical studies of Byron and Joachain on the helium sequence with the numerical functions obtained by McKoy and Winter [12, 15]. A 65 term expansion is taken with the parameter α assigned a value equal to the atomic number, and m, n ranging over 0, 1 to 10, 10 respectively. It is from the compilation of Clementi that the Hartree-Fock functions required have been obtained [16].

In the calculation of the higher partial waves "square root" grids of size 20, 25, 30, 35 and 40 are adopted with the cut-off for the (1*s* 1*s*) pairs being determined as $15/Z$. The cut-off requirement has been gauged from studies upon two electron systems, and investigations in which a variety of choices for the cut off were employed.

Table 1. Partial wave components of $E_2(l)$ for the electron pairs of beryllium, and the third order energies ε^3 (atomic units)

l	Pair $1s\uparrow 1s\downarrow$ $-\varepsilon^2$	Pair $2s\uparrow 2s\downarrow$ $-\varepsilon^2$	Pair $1s\uparrow 2s\downarrow$ $-\varepsilon^2$	Pair $1s\uparrow 2s\uparrow$ $-\varepsilon^2$
0	0.01247	0.00226	0.000522	0.000014
1	0.02248	0.02214	0.001241	0.000663
2	0.00355	0.00382	0.000148	0.000050
3	0.00101	0.00119	0.000041	0.000008
4	0.00039	0.00048	0.000015	0.000002
5	0.00018	0.00023	0.000007	0.6×10^{-6}
6	0.00009	0.00012	0.000003	0.2×10^{-6}
7	0.00005	0.00007	0.000002	0.1×10^{-6}
8	0.00003	0.00004	0.000001	0.5×10^{-7}
9	0.00002	0.00003	0.000001	0.3×10^{-7}
$\geqq 10$	0.00005	0.00007	0.000002	0.4×10^{-7}
Totals	0.04031	0.03044	0.001993	0.000738
$-\varepsilon^3$	0.00205	0.00745	0.000200	0.000100

Table 2. A comparison of the pair correlation energies for beryllium (a.u.)

Source	$-\varepsilon(1s\,1s)$	$-\varepsilon(2s\,2s)$	$-\varepsilon(1s\,2s)$	(Expt. −0.0944)	% $E^{\text{cal}}/E^{\text{obs}}$
Watson[a]	0.03759	0.04178	0.00505	0.08442	89.4
Nesbet[b]	0.04183	0.04535	0.00586	0.09304	98.6
Geller, Taylor, and Levine[c]	0.04208	0.04438	—	0.09143	96.9
Kelly[d]	0.04212	0.04488	0.00497	0.09099	96.4
Szasz and Byrne[e]	0.04235	0.04450	—	0.09182	97.3
Present calculation	0.04236	0.03789	0.00606	0.08631	91.4
Byron and Joachain [9]	0.04247	0.04482	0.00524	0.09253	98.0
Bunge[f]	0.04261	0.04550	0.00530	0.09341	99.0
Tuan and Sinanoğlu[g]	0.04395	0.04392	0.00648	0.09435	99.9

[a] Watson, R. E.: Physic Rev. **119**, 170 (1960).

[b] Nesbet, R. K.: Physic. Rev. **155**, 51 (1967).

[c] Geller, M., Taylor, H. S., Levine, H. B.: J. chem. Physics **43**, 1727 (1965).

[d] Kelly, H. P.: Physic. Rev. **131**, 684 (1963); **136**, 3896 (1964).

[e] Szasz, L., Byrne, W.: Physic. Rev. **158**, 34 (1967).

[f] Bunge, C. F.: Physic. Rev. **168**, 92 (1968).

[g] Tuan, D. F., Sinanoğlu, O.: J. chem. Physics **41**, 2677 (1964).

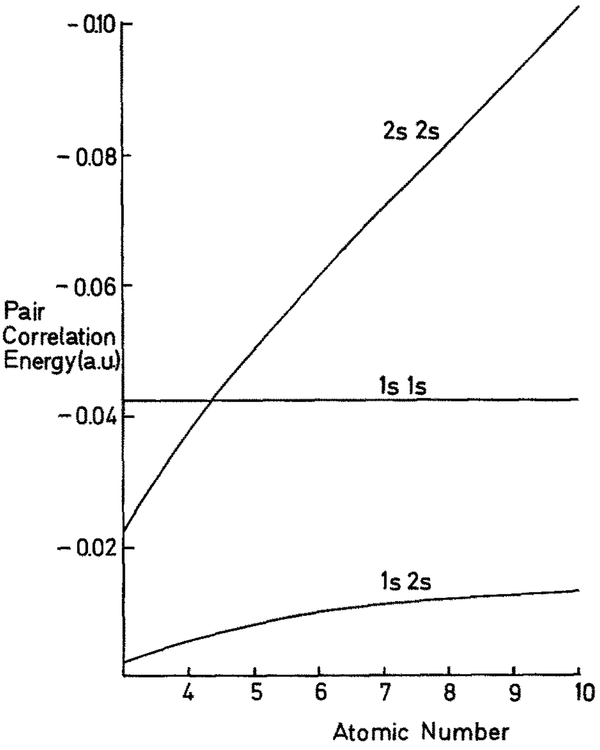

Fig. 1. The variation of the $(1s\,1s)$ $(2s\,2s)$ and $(1s\,2s)$ pair correlation energies (a.u.) with atomic number

Table 3. The pair and total correlation energies of the beryllium sequence (a.u.)

Z Pair	3	4	5	6	7	8	9	10
$-\varepsilon(1s\,1s)$	0.04234	0.04236	0.04233	0.04230	0.04229	0.04228	0.04228	0.04228
$-\varepsilon(2s\,2s)$	0.02232	0.03789	0.05005	0.06118	0.07159	0.08178	0.09164	0.10135
$-\varepsilon(1s\,2s)$	0.00247	0.00606	0.00840	0.00995	0.01102	0.01187	0.01250	0.01299
$-E^{\mathrm{corr}}$	0.06713	0.08631	0.10078	0.11343	0.12491	0.13593	0.14642	0.15662
Expt.[a]	—	0.0944	0.1123	0.1268	0.1412	0.1551	0.1684	0.1814
% $E^{\mathrm{calc}}/E^{\mathrm{obs}}$	—	91.4	89.7	89.5	88.5	87.6	86.9	86.3

[a] Clementi, E.: I.B.M. Journal of Research and Development **9**, 2 (1965).

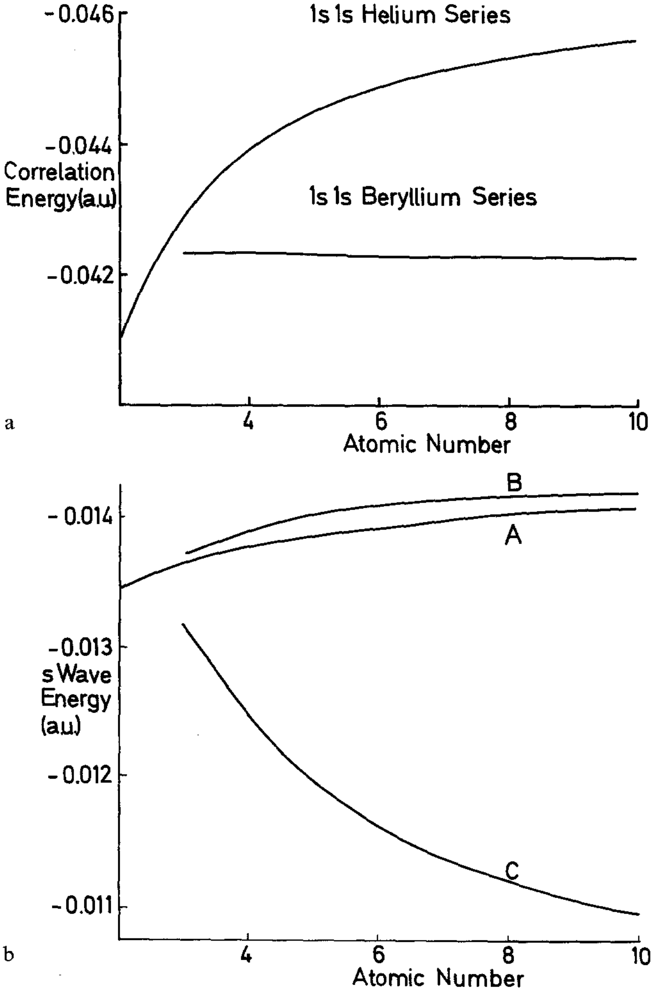

Fig. 2. a The variation of the (1*s* 1*s*) pair correlation energy for the helium isoelectronic sequence as compared with the beryllium sequence (a.u.). b The energy of the *s* wave for the helium sequence and for the beryllium sequence (a.u.). Curve *A*: He sequence. Curve *B*: Be sequence without projection of 2*s* functions. Curve *C*: Be sequence with projection of 2*s* functions

Table 4. Some partial wave contributions to the second order energy for the (1*s* 1*s*) and (2*s* 2*s*) pairs of the Be sequence

Z Pair	3	4	5	6	7	8	9	10
(1*s* 1*s*)								
$\varepsilon^2(l=0)$	−0.01318	−0.01247	−0.01197	−0.01163	−0.01139	−0.01121	−0.01107	−0.01096
$\varepsilon^2(l=1)$	−0.02128	−0.02248	−0.02323	−0.02374	−0.02412	−0.02440	−0.02463	−0.02481
$\varepsilon^2(l=2)$	−0.00344	−0.00355	−0.00362	−0.00367	−0.00370	−0.00373	−0.00375	−0.00376
(2*s* 2*s*)								
$\varepsilon^2(l=1)$	−0.01151	−0.02214	−0.03021	−0.03747	−0.04433	−0.05096	−0.05744	−0.06383
$\varepsilon^2(l=2)$	−0.00241	−0.00382	−0.00449	−0.00491	−0.00519	−0.00541	−0.00557	−0.00570

Amongst the partial waves the *p* wave provides the major component to E^2 the second order energy. For beryllium with $\varepsilon^2(p)$ equal to −0.02248 a.u., and $E2(1s\,1s)$ having a value −0.04031 a.u., the contribution of the *p* wave is 56%. With the third order energy $E^3(1s\,1s)$ for beryllium evaluated to be −0.00205 a.u., the total (1*s* 1*s*) pair correlation energy is −0.04236 a.u. upon the present calculation. That this result is in accord with those obtained by other workers may be seen from Table 2.

The variation in the (1*s* 1*s*) pair correlation energy with atomic number is shown in Fig. 1. In marked contrast to the other pairs, the (1*s* 1*s*) pair energy is almost independent of the atomic number. It is interesting that this behaviour is not found when a (1*s* 1*s*) pair of a two electron sequence is studied. In Fig. 2a the pair correlation energies for the helium isoelectronic sequence is displayed as a function of atomic number. Pair correlation energies for the two electron sequence are obtained in an analagous manner to those for the four electron sequence, using first order Hartree-Fock perturbation theory.

For the two electron atoms the (1*s* 1*s*) pair correlation shows a marked variation with atomic number, an effect which is suppressed when the (1*s* 1*s*) pair is dressed by an outer pair of electrons. The role of the (2*s* 2*s*) electron pair in affecting the correlation energy of the inner pair may be seen in Fig. 2b. As has been noted by others, the outer electron pair exerts its influence primarily through the exclusion principle [9]. If the 2*s* component in the (1*s* 1*s*) pair energy is not projected out, the energy of the *s* wave for the four electron atom follows that of the two electron atom with increase of atomic number. When the 2*s* component is removed, the *s* wave has a higher energy and this term rises with atomic number. The effect is counterbalanced by the higher partial waves in such a manner that the (1*s* 1*s*) pair correlation energy appears to be almost independent of the atomic number. Pertinent data is shown in Table 4.

The (2*s* 2*s*) Pair

The partial wave components of the second order energy for the (2*s* 2*s*) pair of beryllium are listed in Table 1, together with the third order energy. These results are obtained as for the (1*s* 1*s*) pair with the modification that the parameter

α is equated to $Z-2$ and the cut off in the numerical calculation is taken at $33.0/(Z-2)$. The contribution of the s wave to $(2s\,2s)$ pair is seen to be markedly less than in the case of the $(1s\,1s)$ pair. For the p wave the contribution to the total second order energy for the $(2s\,2s)$ pair is now almost totally dominant, being 73% for beryllium. The near degeneracy of $2s^2$ with $2p^2$ is evident.

It is apparent from Table 2 that the pair correlation energy which is obtained for the $(2s\,2s)$ pair of -0.03789 a.u., bears little comparison to other values currently available. The descrepancy stems from the contribution of higher order effects which pass neglected in the first order pair theory. The slow convergence of the Rayleigh-Schrodinger perturbation theory is shown by the fact that for the $(2s\,2s)$ pair of beryllium E^3 is $\sim 24\%$ of E^2 whilst for the $(1s\,1s)$ pair, for which the higher order corrections are likely to be very small, a figure of $\sim 5\%$ is apposite. Should the result for beryllium be compared with that of Byron and Joachain to third order in the energy, then the agreement is seen to be quite favourable. They obtain a value of -0.03803 a.u., which then is complemented by $E^4\,(2s\,2s) = -0.00478$ a.u. and $E^5\,(2s\,2s) = -0.00201$ to give a total $(2s\,2s)$ pair correlation energy of -0.04482 a.u.

In Fig. 1 the near linear variation on the $(2s\,2s)$ pair correlation with atomic number is seen to follow closely the pattern predicted some years ago by Linderberg and Shull and discussed more recently by Alper [17, 18].

The $(1s\,2s)$ Pair

In consideration of the intershell correlation energy the symmetric and antisymmetric components of the s wave have been represented as:

$$\psi^s(r_1 r_2) = \sum_i C_i(r_1^m r_2^n + r_1^n r_2^m)\exp(-\alpha r_1)\exp(-\alpha r_2)\,,$$

$$\psi^A(r_1 r_2) = \sum_i C_i(r_1^m r_2^n - r_1^n r_2^m)\exp(-\alpha r_1)\exp(-\alpha r_2)\,.$$

A forty four term expansion with $\alpha = Z$ was used to represent $\psi^s(r_1 r_2)$ and a forty five term expansion for $\psi^A(r_1 r_2)$. The differences between the results with this function and the more general function noted earlier involving parameters α and β were found to be negligible. In the numerical calculation of the higher waves the cut off is placed at $19.0/Z$ a.u.

The $(1s\,2s)$ pair correlation energy is computed to be -0.00606 a.u. It is to be noted that although values are not given for this quantity under the authors Geller Taylor and Levine, and Szasz, in the total correlation energies which are quoted, a value of -0.00497 a.u. has been incorporated into their results.

As may be seen in Table 2 this is the result of Kelly. Higher values for this quantity -0.00606 a.u. are given by a variety of workers. In our opinion in their calculation of the intershell correlation energy by a variational approach the basis sets employed are not sufficiently flexible. Should the percentage error in the $(1s\,2s)$ pair of beryllium be of the same order of magnitude as is evident when the He$(1s\,2s)$ results of Byron and Joachain, and McKoy and Winter are compared, then the value of -0.00524 quoted for beryllium is too high. Moreover the limit of -0.0053 a.u. by Bunge is likely to be exceeded. Recently Pan and King [19] have obtained second order energies for the $(1s\,2s)$ pair which are substantially

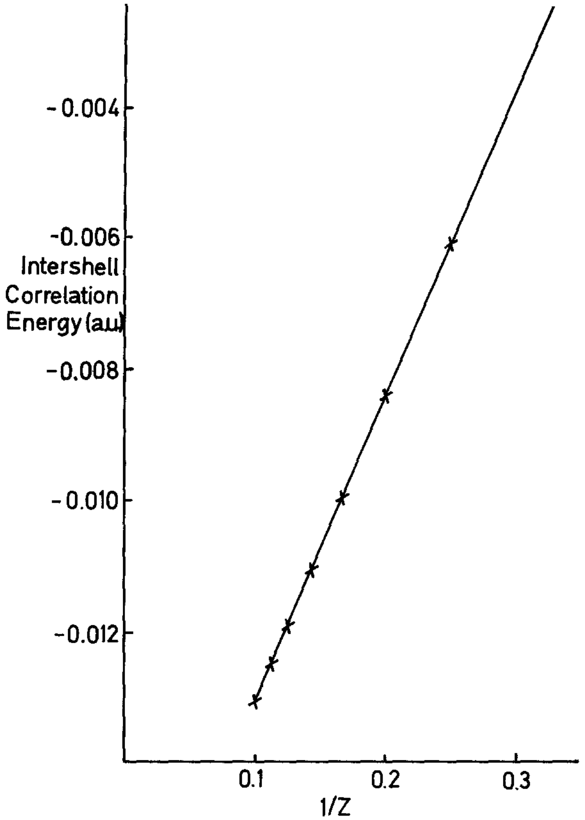

Fig. 3. The intershell correlation energy for the beryllium sequence as a function of $1/Z$ (a.u.)

larger in magnitude than those of Byron and Joachain, in accord with the viewpoint propagated here.

As the atomic number varies from lithium to neon, the intershell correlation energy follows the behaviour depicted in Fig. 1. In Fig. 3 it is shown that this variation is near to linear in $1/Z$. Miller and Ruedenberg have observed this relationship within an augmented separated pair calculation [20].

It was Schwartz who pointed out that the energy $E(l)$ for singlet states should vary with l as l^{-4} and a guess was made that for the triplet states "the asymptotic rate of decrease would be l^{-6}" [10]. In Fig. 4 the function $\log|\varepsilon^2(l)|$ is plotted against $\log l$. The behaviour for the triplet portion of the $(1s\,2s)$ pair is indeed seen to converge on the line of slope 6 whilst the singlet states of the $(1s\,1s)$, $(1s\,2s)$ and $(1s\,2s)$ pairs follow the line of slope 4. The contribution of partial waves for $l \geqq 10$ has been estimated on the basis of this behaviour.

Concluding Discussion

One of the purposes of this study has been to find an efficient technique with respect to time of computation and accuracy in calculation for obtaining pair functions for atoms. An ultimate objective is to be able to compute two

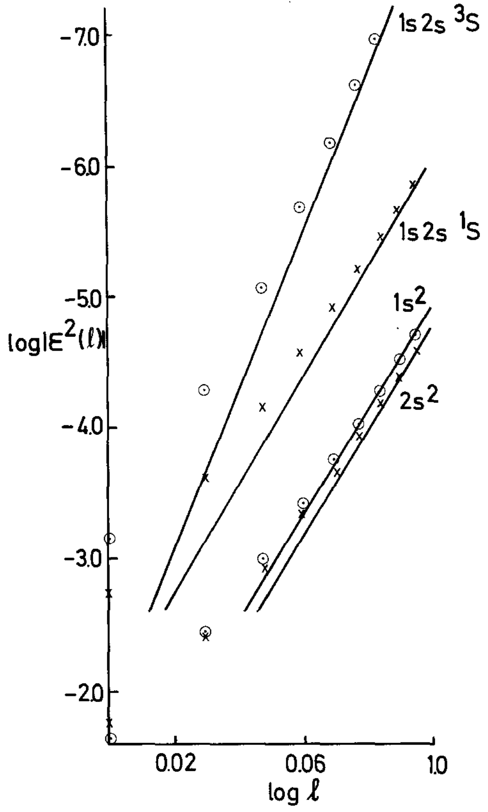

Fig. 4. The asymptotic behaviour of the second order energy

electron functions for atoms of any atomic number. In 1962 Szasz wrote "we shall be able to apply the theory of correlated wave functions to the calculation of wave functions for atoms with any number of electrons". That this is possible in principle may be correct, yet in the ensuing ten years no solutions for other than light atoms have appeared.

A combination of the variational perturbation approach and a numerical approach when the trial functions are represented by a Legendre expansion would seem to offer a tractable route to the evaluation of pair functions. In the four electron sequence studied the first order pair equations have been solved to quite a high order of accuracy without excessive computation time. The central deficiency, as has been remarked, lies in the need for including higher order effects for the ($2s\,2s$) pair. The calculations have not been extended in this fashion, since it is not felt that for chemical purposes there is a vital need to seek the remaining 10% of the correlation energy. It may be seen from Table 3 that 86–91% of the correlation energy has been accounted for by the present calculations in a situation where a $2p^2$ configuration lies in close proximity to the ground state.

To support such a viewpoint one might consider the calculation of the electron affinity of lithium. On the basis of a Hartree-Fock calculation this is evaluated to be -0.12 eV [16]. With the energy of Li taken to be -7.47807 a.u. which is the result of Weiss, a value of +0.47 eV is found for the electron affinity [20]. The experimental value is cited to be 0.6 eV or alternatively lies between the limits 0.65 eV and 1.05 eV [22, 23]. Should one estimate that the error in the $(2s\,2s)$ pair energy is of the order ~ 0.1 eV, the former value observed is matched, when one allows ~ 0.03 eV for additional terms which pass neglected. A recent study by Victor and Laughlin yields 0.591 eV for the electron affinity of lithium, strengthening the view that the experimental result of Ya'Akobi is to be preferred [24].

In the early calculations of Hartree upon atomic wave functions numerical techniques played a dominant role. For a period of time now they have passed out of fashion. This is a pity for they are indeed a powerful device in computing atomic properties. The manner in which the computation of single centre molecular expansions, and of atomic polarisabilities is facilitated with numerical techniques will be the subject of subsequent papers. Calculations upon other atomic systems also are in progress.

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