1966

Electron correlation, pair approximation and augmented pair expansion: application to beryllium-like atomic systems

Kenneth John Miller
Iowa State University

Recommended Citation

Miller, Kenneth John, "Electron correlation, pair approximation and augmented pair expansion: application to beryllium-like atomic systems " (1966). *Retrospective Theses and Dissertations*. 2871.
https://lib.dr.iastate.edu/rtd/2871

66–6992

MILLER, Kenneth John, 1939–

ELECTRON CORRELATION, PAIR APPROXIMATION AND AUGMENTED PAIR EXPANSION. APPLICATION TO BERYLLIUM-LIKE ATOMIC SYSTEMS.

Iowa State University of Science and Technology
Ph.D., 1966
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

ELECTRON CORRELATION, PAIR APPROXIMATION AND AUGMENTED PAIR EXPANSION. APPLICATION TO BERYLLIUM-LIKE ATOMIC SYSTEMS

by

Kenneth John Miller

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1966

TABLE OF CONTENTS

Page

PART I. THE SEPARATED PAIR APPROXIMATION 1

INTRODUCTION 2

GLOSSARY 6

WAVEFUNCTION AND ENERGY IN THE SEPARATED PAIR APPROXIMATION 7

- Separated Pair Approximation, Separated Geminals, Natural Orbitals 7
- Energy Expression 8
- Variational Equations 10
- Determination of Geminals 12

SEPARATED PAIR APPROXIMATION FOR BERYLLIUM-LIKE SYSTEMS 18

- General Form of Geminals 18
  - Expansion in Slater-type atomic orbitals 18
  - Transformation matrix T 19
  - Separated pair approximations to different degrees of accuracy 21
- Optimal Geminals 21
  - Natural orbitals 21
  - Occupation coefficients 23
  - Principal natural orbitals and Hartree-Fock approximation 24
- Energy 25
  - Correlation energy recovered 25
  - Comparison with other investigations 27
  - Correction for K-geminal defect 28
- Comparison with Calculations Based on Sinanoğlu's Theory 29

ENERGY ANALYSIS IN THE SEPARATED PAIR APPROXIMATION 34

- General Partitioning and Correlation Energy 34
- Quantitative Discussion of Beryllium-like Systems 39
- Secondary Natural Orbitals, Dynamical and Non-dynamical Correlation 41
- Comparison with Other Methods of Analysis 45

Page

INTERELECTRONIC COORDINATES IN THE PAIR APPROXIMATION FOR BERYLLIUM 47

Object and Scope 47
Method 49
Results 50

PART II. AUGMENTED SEPARATED PAIR EXPANSION 53

INTRODUCTION 54

GLOSSARY 57

WAVEFUNCTION AND ENERGY IN THE AUGMENTED SEPARATED PAIR EXPANSION 58

Expansion in Spin Harmonics and Geminal Products 58

Expansion in terms of spin functions 58
Reduction with respect to geminal subgroups 59
Expansion of space functions 61
Expansion in terms of geminal products 62

Augmented Separated Pair Expansion 65

Augmented separated pair configurations 65
Essential augmented separated pair configurations 69
Energy analysis of augmented separated pair expansion 71

AUGMENTED SEPARATED PAIR EXPANSION FOR BERYLLIUM-LIKE SYSTEMS 75

Construction of Wavefunction 75

Space-spin functions 75
The ^1S state 76
Determination of important configurations 78
Characteristics of contributing configurations 81

Quantitative Results 83

Energy and expansion coefficients 83
Intergeminal correlations 84
Perturbation theory 87

Page

LITERATURE CITED 89

ACKNOWLEDGMENTS 95

APPENDIX 96

LIST OF FIGURES

Figure		Page
1	Effect on energy of using maximum number of natural orbitals in separated pair approximations to the beryllium atom wavefunction	97
2	Effect on energy of optimizing the transformation matrix T in separated pair approximations to the beryllium atom wavefunction	98
3	Energy lowering due to addition of various natural orbitals to separated pair approximations of the beryllium atom wavefunction	99
4	Natural orbitals used with each geminal for various separated pair approximations in this investigation	100
5	Orbital exponents of Slater-type atomic orbitals used in various separated pair approximations to the beryllium-like atomic wavefunctions	101
6	Polynomial approximations to orbital exponents	102
7	Scale factors for various separated pair approximations to beryllium-like atomic wavefunctions	103
8	Expansion coefficients of natural orbitals of separated pair approximation Φ_2 in terms of Schmidt orthogonalized Slater-type atomic orbitals	104
9	Expansion coefficients of natural orbitals of separated pair approximation Φ_3 in terms of Schmidt orthogonalized Slater-type atomic orbitals	106
10	Expansion coefficients of natural orbitals of separated pair approximation Φ_4 in terms of Schmidt orthogonalized Slater-type atomic orbitals	108
11	Natural orbital occupation coefficients for separated pair approximations to beryllium-like atomic wavefunctions	112
12	Occupation numbers of separated pair approximation Φ_4 for beryllium, nitrogen +3 and neon +6	113
13	Comparison between the antisymmetrized product of the first two natural orbitals and the Hartree-Fock wavefunction	114

Figure Page

14 Energies of various separated pair approximations for beryllium-like atoms 115

15 K-geminal defect of two-electron systems 116

16 Energy analysis of separated pair approximations for lithium -1 117

17 Energy analysis of separated pair approximations for beryllium 118

18 Energy analysis of separated pair approximations for boron +1 119

19 Energy analysis of separated pair approximations for carbon +2 120

20 Energy analysis of separated pair approximations for nitrogen +3 121

21 Energy analysis of separated pair approximations for oxygen +4 122

22 Energy analysis of separated pair approximations for fluorine +5 123

23 Energy analysis of separated pair approximations for neon +6 124

24 Analysis of electronic energy of Ebbing and Henderson's separated pair approximation for lithium hydride 125

25 Comparison of shell correlations for the beryllium atom 126

26 Wavefunction and energies of various pair approximations containing interelectronic distances for beryllium 127

27 Classification of essential augmented separated pair configurations according to natural orbital geminals 128

28 Energies of various augmented separated pair expansions for beryllium-like atoms 129

29 Coefficients of augmented separated pair configurations in the augmented separated pair expansion Ψ_2 for beryllium-like atoms 130

Figure Page

30 Coefficients of augmented separated pair configurations in the augmented separated pair expansion Ψ_3 for beryllium-like atoms 131

31 Coefficients of augmented separated pair configurations in the augmented separated pair expansion Ψ_4 for beryllium-like atoms 132

32 Energy analysis of augmented separated pair expansion Ψ_2 for beryllium-like atoms 133

33 Energy analysis of augmented separated pair expansion Ψ_3 for beryllium-like atoms 134

34 Energy analysis of augmented separated pair expansion Ψ_4 for beryllium-like atoms 135

35 Comparative analysis of energy lowering of ASPE's and comparison with perturbation theory 136

36 Comparison between variational calculation and perturbation calculation for beryllium for augmented separated pair expansion Ψ_3 137

LIST OF GRAPHS

Graph		Page
1	Analysis of intrageminal contributions to energy lowering in the separated pair approximation	138
2	Dependence upon nuclear charge of intrageminal and intergeminal contributions to energy lowering in the separated pair approximation	140
3	Energy lowering due to intergeminal correlations for the augmented separated pair expansion	141

PART I. THE SEPARATED PAIR APPROXIMATION

INTRODUCTION

In recent years, the successful progress of ab initio calculations for atoms and small molecules has been encouraging. Particularly impressive have been the determinations of practically exact Hartree-Fock wavefunctions for atoms and diatomic molecules. This convincing work has proved that the self-consistent field approximation can be of chemical use only in conjunction with a set of reliable rules for the accurate estimation of correlation errors, if such rules can be established. The feasibility of ab initio calculations beyond the Hartree-Fock approximation has therefore become of considerable interest, a fact which is attested to by Sinanoğlu's remarkable work.

The theory of separated electron pairs goes back to Hurley's thesis (1952) and the paper by Hurley, Lennard-Jones and Pople (1953). Although the idea of using antisymmetrized products of pair functions had been alluded to previously by Pauling (1949), by Fock (1950) and perhaps even earlier by others, it was the paper by Hurley et al. which introduced the crucial element in the theory: the concept of strong orthogonality. Specifically, these authors formulated the following three ideas:

(i) Any two geminals Λ_μ, Λ_ν satisfy the strong orthogonality condition

$$\int dV_1 \Lambda_\mu^*(1,2)\Lambda_\nu(1,3) = 0, \quad \mu \neq \nu.$$

(ii) These are equivalent to the orbital orthogonalities

$$\int dV_1 u_{\mu i}^*(1) u_{\nu k}(1) = 0, \ \mu \neq \nu, \quad \text{for all } i,k$$

if Λ_μ and Λ_ν are given by the expressions

$$\Lambda_\mu(1,2) = \sum_{i,k} a_{ik}{}^{\mu} u_{\mu i}(1) u_{\mu k}^*(2),$$

$$\Lambda_\nu(1,3) = \sum_{i,k} a_{ik}{}^{\nu} u_{\nu i}(1) u_{\nu k}^*(3).$$

(iii) Without loss of generality any pair function can be written in the "diagonal form"

$$\Lambda_\mu(1,2) = \sum_i C_{\mu i} \phi_{\mu i}(1) \phi_{\mu i}^*(2)$$

with

$$\int dV_1 \phi_{\mu i}^*(1) \phi_{\nu j}(1) = 0, \quad \mu \neq \nu, \text{ for all } i,j.$$

The important simplification achieved by these assumptions is that only interactions within one geminal and between any two geminals enter the energy expectation value.

Various authors have subsequently re-examined the separated pair approximation. Parks and Parr (1958) suggested that it may be helpful to minimize the energies of the individual geminals turn by turn, since they are easily isolated in the total energy expression. The same authors also considered the adaptation to semiempirical usage. Sets of coupled integrodifferential equations were derived for the two-electron functions by Kapuy (1958, 1960a) and for the natural orbitals by Kutzelnigg (1964) who also considered a method for determining the natural orbitals as well as the occupation coefficients. Incorrect equations for the geminals were given by Parks and Parr. Recently McWeeny (1959, 1960) and McWeeny and Mizuno (1961) developed a theory of generalized group functions of which the separated pair approximation is a special case.

The attempt by Kapuy (1959, 1960b, 1961b) to develop a theory of electron pairs with "almost orthogonal" two-electron functions has yielded equations which appear impractical for actual work. The work by Szász (1959, 1960, 1962a, 1962b, 1963b) with non-orthogonal two-electron functions containing interelectronic distances has led to many types of complex matrix elements containing interelectronic distances and connecting the coordinates of more than two electrons.

Although the separated pair approximation was proposed more than a decade ago, only very few rigorous implementations have been attempted so far, namely the work by Ebbing and Henderson (1965) on the lithium hydride molecule, the work by McWeeny and Ohno (1960) on the water molecule and that by McWeeny and Sutcliffe (1963) on the beryllium atom. In all three cases, very limited basis sets were used and various additional simplifying assumptions very severely restricted the variational possibilities. For this reason, the full potential of the separated pair approximation in the context of the *ab initio* calculations has thus far remained unexplored.

In the present investigation, a method is developed which permits the general determination of the separated pair approximation by a variational procedure and which leads directly to its natural orbitals. The method is then applied to the ground states of the iso-electronic series of the atomic systems containing four electrons. Uniformly, about 90 per cent of the correlation energy is recovered; but it is suspected that with somewhat more favorable computational equipment this may perhaps be increased to 92 per cent. The understanding of the source of the correlation energy is a further objective of the investigation. It is achieved by an analysis based on a partitioning of the energy into contributions from various geminals and various natural orbitals. From this analysis a variety of inferences for future applications are drawn.

In spite of the very considerable improvement over the Hartree-Fock approximation, the separated pair approximation is probably not quite good enough to yield absolute energies of chemical accuracy, if the latter is defined to be about 1 kcal or about 10^{-3} a.u. However, it is here proposed that the separated pair approximation can be taken as an excellent zeroth-order approximation which may be ideally suited for including all further improvements as very small additive corrective terms. This question will be taken up in Part II.

GLOSSARY

Although all abbreviations are defined in the text, the following list may be helpful.

AP	antisymmetrized product
APG	antisymmetrized product of geminals
APSG	antisymmetrized product of separated geminals
SPA	separated pair approximation
Φ_{SP}	wavefunction corresponding to the exact SPA
Φ_i, APSG Φ_i	the i-th approximation to Φ_{SP}
$\tilde{\Phi}_i$, APG $\tilde{\Phi}_i$	the i-th approximation to APG
STAO	Slater-type atomic orbital
NO	natural orbital
PNO	principal natural orbital
HF	Hartree-Fock

WAVEFUNCTION AND ENERGY IN THE SEPARATED PAIR APPROXIMATION

Separated Pair Approximation, Separated Geminals, Natural Orbitals

Within the pair approximation the wavefunction of a 2n-electron system is defined as the antisymmetrized product of geminals (APG)

$$\Phi(1,2,\ldots 2n) = \mathcal{A}\{\Lambda_1(1,2)\theta_1(1,2)\ldots\Lambda_\nu(2\nu-1,2\nu)\theta_\nu(2\nu-1,2\nu)\ldots \Lambda_n(2n-1),2n)\theta_n(2n-1,2n)\}, \qquad (1.1)$$

where the geminals Λ_γ, $\gamma = 1,2,\ldots\nu,\ldots n$ and the associated spin functions θ_γ are dictated by the physical situation and $\mathcal{A}$ is the partial antisymmetrizer

$$\mathcal{A} = [2^n/(2n)!]^{\frac{1}{2}} \sum_P (-1)^P P, \qquad (1.2)$$

where the operator P permutes electron coordinates between different two-electron space-spin products only. Each two-electron space-spin product is antisymmetric with respect to interchange of coordinates. Without loss of generality it can be assumed

(i) that the geminals are weakly orthogonal and normalized to unity

$$\int dV_1 \int dV_2 \Lambda_\mu^*(1,2)\Lambda_\nu(1,2) = \delta_{\mu\nu}, \qquad (1.3)$$

(ii) that each geminal is expressed as a natural expansion

$$\Lambda_\mu(1,2) = \sum_i C_{\mu i}\phi_{\mu i}(1)\phi_{\mu i}^*(2) \qquad (1.4)$$

with

$$\int dV \phi_{\mu i}^* \phi_{\mu j} = \delta_{ij}, \qquad (1.5)$$

(iii) that the $\phi_{\gamma i}$ are real if Λ_γ is symmetric in its two electron coordinates.

Separated geminals are characterized by the strong orthogonality condition

$$\int dV_1 \Lambda_\mu^*(1,i)\Lambda_\nu(1,j) = 0 \quad (\mu \neq \nu). \qquad (1.6)$$

With this additional constraint, the wavefunction Φ of Equation 1.1 is referred to as separated pair approximation or as an antisymmetrized product of separated geminals, hereafter abbreviated as APSG. By virtue of Equations 1.3 and 1.6, Φ is then normalized to unity.

Arai (1960), Löwdin (1961) and more recently Kutzelnigg (1964) have shown that if two geminals are strongly orthogonal, all natural orbitals of one are orthogonal to all natural orbitals of the other. In other words, if $(\phi_{\gamma 1},\phi_{\gamma 2},\ldots)$ are the natural orbitals of geminal $\Lambda_\gamma (\gamma = K,L,M,\ldots)$ then the set $(\phi_{K1},\phi_{K2},\ldots;\phi_{L1},\phi_{L2},\ldots;\phi_{M1},\phi_{M2},\ldots)$ forms an orthonormal basis which can be generated from an arbitrary complete orthonormal basis $(\chi_1,\chi_2,\chi_3,\ldots)$ by a certain isometric transformation T, i.e.,

$$(\phi_{K1},\phi_{K2},\ldots;\phi_{L1},\phi_{L2},\ldots;\phi_{\mu 1},\phi_{\mu 2},\ldots) = (\chi_1,\chi_2,\chi_3,\ldots)T. \qquad (1.7)$$

It furthermore follows that in the separated pair approximation, the set of all natural orbitals of all geminals is identical with the set of all natural orbitals of the wavefunction Φ.

Energy Expression

If the non-relativistic Hamiltonian of the electrons $i=1,2,\ldots 2n$ in the field of the nuclei $\alpha=1,2,\ldots A$ is written as

$$H = \sum_i h(i) + \sum_{i<j} r_{ij}^{-1}, \tag{1.8}$$

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_\alpha Z_\alpha r_{\alpha i}^{-1}, \tag{1.8$'$}$$

then the non-relativistic energy calculated with the Separated Pair Approximation 1.1 is given by

$$\begin{aligned} E &= (\Phi|H|\Phi) \\ &= \sum_\mu \{ 2 \sum_i C_{\mu i}^2 (\mu i|\mu i) + \sum_{i,j} C_{\mu i} C_{\mu j} [\mu i,\mu j|\mu j,\mu i] \} \\ &+ \sum_{\mu<\nu} \{ \sum_{i,j} C_{\mu i}^2 C_{\nu j}^2 (4[\mu i,\mu i|\nu j,\nu j] - 2[\mu i,\nu j|\nu j,\mu i]) \} \end{aligned} \tag{1.9}$$

where the following definitions have been introduced:

$$(\alpha|\beta) = \int dV \phi_\alpha^* h \phi_\beta \tag{1.10}$$

$$[\alpha,\beta|\gamma,\delta] = \int dV_1 \int dV_2 \phi_\alpha^*(1)\phi_\beta(1)\phi_\gamma^*(2)\phi_\delta(2) r_{12}^{-1} \tag{1.11}$$

For future reference the energy expression is written also as

$$E = \sum_\mu E(\mu) + \sum_{\mu<\nu} I(\mu,\nu) \tag{1.12}$$

where the $E(\mu)$'s represent <u>intrageminal energies</u> and the $I(\mu,\nu)$'s represent <u>intergeminal interaction energies</u>. Every intrageminal energy $E(\mu)$ is a sum over the natural orbital contributions:

$$E(\mu) = \sum_{i,j} C_{\mu i} C_{\mu j} \mathcal{E}(\mu i,\mu j) \tag{1.13}$$

where

$$\mathcal{E}(\mu i,\mu j) = 2(\mu i|\mu i)\delta_{ij} + [\mu i,\mu j|\mu j,\mu i]. \tag{1.14}$$

Every intergeminal energy $I(\mu,\nu)$ is a sum of contributions from intergeminal orbital-pairs:

$$I(\mu,\nu) = \sum_{i,j} C_{\mu i}{}^2 C_{\nu j}{}^2 \mathcal{J}(\mu i,\nu j) \tag{1.15}$$

where

$$\mathcal{J}(\mu i,\nu j) = 4[\mu i,\mu i|\nu j,\nu j] - 2[\mu i,\nu j|\nu j,\mu i]. \tag{1.16}$$

The <u>total energy of a geminal within the system</u> is given by

$$\epsilon_\mu = E(\mu) + I(\mu) \tag{1.17}$$

where

$$\begin{aligned} I(\mu) &= \sum_{\nu(\neq\mu)} I(\mu,\nu) \\ &= \sum_i C_{\mu i}{}^2 \mathcal{J}(\mu i), \end{aligned} \tag{1.18}$$

with

$$\mathcal{J}(\mu i) = \sum_{\nu(\neq\mu)} \sum_j C_{\nu j}{}^2 \mathcal{J}(\mu i,\nu j), \tag{1.19}$$

represents the interaction between the μth geminal and all other geminals. Using the geminal energies ϵ_μ, the total energy of the system can also be be expressed in the two forms:

$$E = \sum_\mu \epsilon_\mu - \sum_{\mu<\nu} I(\mu,\nu), \tag{1.20}$$

$$E = \frac{1}{2} \sum_\mu \{E(\mu) + \epsilon_\mu\}. \tag{1.21}$$

Variational Equations

Independent variations of the energy expression with respect to the natural orbitals and occupation coefficients lead to two interdependent sets of equations.

Variation of the natural orbital occupation coefficients results in the following set of coupled eigenvalue equations for each separated geminal (McWeeny and Sutcliffe, 1963 and Kutzelnigg, 1964):

$$\sum_j H_{ij}{}^{\mu} C_{\mu j} = \epsilon_\mu C_{\mu i} \qquad (i = 0,1,\ldots) \qquad (1.22)$$

where

$$H_{ij}{}^{\mu} = \mathcal{E}(\mu i,\mu j) + \mathcal{J}(\mu i)\delta_{ij} \qquad (1.23)$$

represents an effective electron pair Hamiltonian matrix for the μth geminal. The eigenvalue ϵ_μ is readily shown to be identical with the total geminal energy defined in Equation 1.17. The coupling matrix $\mathcal{J}(\mu i)$ defined by Equation 1.19 couples the eigenvalue equation for the μth geminal with the eigenvalue equations of all other geminals.

Variation of the natural orbitals yields the set of integrodifferential equations

$$\{C_{\mu i}{}^2 F_{\mu i} + \sum_{j(\neq i)} C_{\mu i} C_{\mu j} K_{\mu j}\}\phi_{\mu i} = \sum_\nu \sum_j \lambda_{\mu i,\nu j}\phi_{\nu j}, \quad (i=1,2,\ldots) \qquad (1.24)$$

for each separated geminal (Kutzelnigg, 1964) where

$$F_{\mu i} = h + K_{\mu i} + \sum_{\nu(\neq\mu)} \sum_j C_{\nu j}{}^2\{2J_{\nu j} - K_{\nu j}\}, \qquad (1.25)$$

$$J_{\mu i}(1) = \int dV_2 \phi_{\mu i}{}^*(2)\phi_{\mu i}(2) r_{12}{}^{-1}, \qquad (1.26)$$

$$K_{\mu i}(1)\phi(1) = \int dV_2\{\phi_{\mu i}(1)\phi_{\mu i}{}^*(2) r_{12}{}^{-1}\}\phi(2); \qquad (1.27)$$

and, $\lambda_{\mu i,\nu j}$ is a Lagrange multiplier incorporating the constraints

$$\int dV \phi_{\mu i}^{*} \phi_{\nu j} = \delta_{\mu\nu} \delta_{ij} \, . \tag{1.28}$$

A different formulation of these variational equations has been developed by Huzinaga (1964).

The Integrodifferential Equations 1.24 can be used to derive a cusp condition for the natural orbitals in the special case that the first order density matrix is invariant under rotations as, e.g., for certain atomic states. In this case, the natural orbitals are symmetry orbitals and can be classified according to quantum numbers ℓ and m. It is found that their radial parts $R_{\mu i}(r)$ satisfy the cusp conditions

$$\bar{R}'_{\mu i}(0)/\bar{R}_{\mu i}(0) = -Z/(\ell+1) \tag{1.29}$$

if

$$R_{\mu i}(r) = r^{\ell} \bar{R}_{\mu i}(r), \tag{1.30}$$

ℓ being the angular momentum quantum number.

Determination of Geminals

The determination of the geminals implies finding the natural orbitals and the natural orbital occupation coefficients. They are determined as simultaneous solutions of Equations 1.22 and 1.24 which are mutually dependent. If each equation were solvable separately, then one would hope to converge to the correct solution by shuttling back and forth between the two.

In practice the set of coupled eigenvalue equations for the coefficients, as given by Equation 1.22, can be solved by an iterative sequence of eigenvalue calculations for the different geminals, and this procedure is adopted here. The equation for the natural orbitals, Equation 1.24, on the other hand, appears somewhat unwieldy for practical work, especially in view of the off-diagonal Lagrangian multipliers. An alternative method, based on a direct energy minimization, was therefore developed and used here.

In the present approach, the natural orbitals are constructed by an orthogonal transformation T from an arbitrarily, but judiciously, chosen set of orthonormal basis orbitals χ_i in accord with Equation 1.7. Furthermore, these basis functions are allowed to contain certain adjustable, in general non-linear, orbital parameters ζ_i. (The specific basis orbitals used in the present work are orthogonalized Slater-type atomic orbitals, the ζ_i being the orbital exponents; but this is not essential for the described method. Under these premises the determination of the natural orbitals is equivalent to

(i) making the appropriate choice of the basis χ_i,

(ii) finding the appropriate orbital parameters ζ_i,

(iii) finding the appropriate matrix T;

and it is clear that the solution of Equation 1.24 can be replaced by a minimization of the total energy for fixed occupation coefficients with respect to variations of the orbitals χ_i, of the orbital parameters ζ_i and of the matrix elements T_{ij}.

In the interest of saving computer time, a slightly more involved iterative scheme was adopted. It consists of two main parts which are executed in alternation. In Part I the parameters ζ_i are fixed; T and the $C_{\mu i}$ are changed. In Part II the matrix T is fixed, and the ζ_i and

$C_{\mu i}$ are changed.

The basic cycle of Part I consists of two steps. The first step is an improvement of T by multiplication with another orthogonal matrix. If the current value of T is $T^{(n)}$ the improved value will be $T^{(n+1)} = T^{(n)}R(\theta)$ where $R(\theta)$ is a two by two rotation

$$R(\theta) = \begin{pmatrix} R_{ii} & R_{ij} \\ R_{ji} & R_{jj} \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \tag{1.31}$$

corresponding to a certain index pair (i,j). The angle θ is determined by minimizing the total energy, while the orbital parameters as well as the occupation coefficients are kept constant. The details of the minimization are outlined below. The change in T leads to new natural orbitals and, with these new orbitals kept fixed, the second step consists of solving the Eigenvalue Equations 1.22 to find a new set of occupation coefficients $\bar{C}_{\mu i}$. This basic cycle is executed sequentially for all index pairs (i,j) and repeated until no further energy lowering is found.

Part II of the technique is a minimization of the energy function $\tilde{E}(T, \zeta_i)$ with respect to the non-linear parameters ζ_i while T is kept fixed. This energy function is defined as follows: Determine the coefficients $C_{\mu i}$ from the Eigenvalue Equation 1.22 for fixed T and ζ_i's and substitute them in the total energy expression, which becomes a function of T and ζ_i alone. The minimization of $\tilde{E}(T,\zeta_i)$ can be executed by any one of the iterative techniques for minimization with respect to non-linear parameters (Ransil, 1960, Spang, 1962 and Wasserman, 1963). In practice the pattern search method (Hooke and Jeeves, 1961) was used.

The details of the two by two rotation mentioned above are as follows: Let $\phi_{\mu i}$ be the natural orbital obtained from the orthogonal matrix $T^{(n)}$, i.e.,

$$(\ldots\phi_{\mu i},\ldots) = (\chi_1,\chi_2,\ldots)T^{(n)} \tag{1.32}$$

and let $\psi_{\alpha i}$ be the natural orbitals obtained from the matrix

$$T^{(n+1)} = T^{(n)}R(\theta), \tag{1.33}$$

i.e.,

$$(\ldots\psi_{\alpha i},\ldots) = (\chi_1,\chi_2,\ldots)T^{(n)}R(\theta) \tag{1.34}$$

where $R(\theta)$ is the two by two matrix given in Equation 1.31. Let $E^{(n)}$ be the total energy calculated with orbitals $\phi_{\mu i}$ and let $E^{(n+1)}$ be that obtained from the orbitals $\psi_{\alpha i}$. A straightforward calculation of the energy difference yields the expression

$$\Delta E = E^{(n+1)}-E^{(n)} = \sum_{k=1}^{4} q_k \sin^k\theta\cos^{4-k}\theta \tag{1.35}$$

where the constants q_k are defined as follows:

$$q_4 = A_{\mu\nu} + b_1\{[\mu i,\mu i|\mu i,\mu i]-2[\mu i,\nu j|\nu j,\mu i]+[\nu j,\nu j|\nu j,\nu j]\}, \tag{1.36}$$

$$q_3 = B_{\mu\nu} - 4b_1\{[\mu i,\mu i|\nu j,\mu i] - [\nu j,\nu j|\mu i,\nu j]\}, \tag{1.36$'$}$$

$$q_2 = A_{\mu\nu} + 2b_1\{[\mu i,\mu i|\nu j,\nu j] + [\mu i,\nu j|\mu i,\nu j]\}, \tag{1.36$''$}$$

$$q_1 = B_{\mu\nu} \tag{1.36$'''$}$$

where

$$\begin{aligned}
b_0 &= 8C_{\mu i}{}^2 C_{\nu j}{}^2 (1-\delta_{\mu\nu}), \\
b_1 &= C_{\mu i}{}^2 + C_{\nu j}{}^2 - 2C_{\mu i}C_{\nu j}\delta_{\mu\nu} - 2C_{\mu i}{}^2 C_{\nu j}{}^2 (1-\delta_{\mu\nu}), \\
b_2 &= C_{\mu i}{}^2 - C_{\nu j}{}^2
\end{aligned}$$

and

$$\begin{aligned}
A_{\mu\nu} = {}& -b_0\{[\nu j,\mu i|\mu i,\nu j] - [\mu i,\mu i|\nu j,\nu j]\} + 2b_2\{(\nu j|\nu j)-(\mu i|\mu i)\} \\
& + 2C_{\mu i}\{X_\mu(\nu j,\nu j) - X_\mu(\mu i,\mu i)\} - 2C_{\nu j}\{X_\nu(\nu j,\nu j) - X_\nu(\mu i,\mu i)\} \\
& + C_{\mu i}{}^2\{Y_\mu(\nu j,\nu j) - Y_\mu(\mu i,\mu i)\} - C_{\nu j}{}^2\{Y_\nu(\nu j,\nu j) - Y_\nu(\mu i,\mu i)\},
\end{aligned}$$

$$\begin{aligned}
B_{\mu\nu} = {}& 4b_2(\mu i|\nu j) \\
& + 4\{C_{\mu i}X_\mu(\mu i,\nu j) - C_{\nu j}X_\nu(\mu i,\nu j)\} \\
& + 2\{C_{\mu i}{}^2 Y_\mu(\mu i,\nu j) - C_{\nu j}{}^2 Y_\nu(\mu i,\nu j)\},
\end{aligned}$$

with

$$\begin{aligned}
X_\mu(\kappa i,\lambda j) &= \sum_m C_{\mu m}[\kappa i,\mu m|\mu m,\lambda j], \\
Y_\mu(\kappa i,\lambda j) &= \sum_{\gamma(\neq\mu)} \sum_m C_{\gamma m}{}^2 \{4[\gamma m,\gamma m|\kappa i,\lambda j] - 2[\kappa i,\gamma m|\gamma m,\lambda j]\}.
\end{aligned}$$

All integrals are understood to be between the orbitals $\phi_{\mu i}$ existing before multiplying by $R(\theta)$. These relations are formulated for an intergeminal rotation. The relation for intrageminal rotations are simply obtained by the substitutions of $\phi_{\mu j}$ for $\phi_{\nu j}$ and $C_{\mu j}$ for $C_{\nu j}$ which result in certain simplifications. The energy minimum occurs when θ satisfies

$$\frac{\partial E}{\partial \theta} = 0 = -s^4 q_3 + s^3 c(4q_4 - 2q_2) + 3s^2 c^2 (q_3 - q_1) + 2sc^3 q_2 + c^4 q_1 \quad (1.37)$$

where $s = \sin \theta$ and $c = \cos \theta$. In all cases examined so far, only one minimum seemed to exist. Its position relative to the origin ($\theta = 0$) is determined by the sign of q_1. The method of two by two rotation has been applied to helium by Reid and Öhrn (1963). Equations 1.36 to 1.36‴ simplify to their formulas for the helium atom.

The actual calculations to be reported in the next section show that minimization with respect to all three types of parameters is essential for making most effective use of a given basis set. Much poorer results would be obtained if, as Parks and Parr (1958) have suggested, one would in advance rigidly divide the linear space spanned by all orbitals into several, fixed, mutually orthogonal subspaces, one for each shell. To be sure, such a subdivision has the simplifying feature that the only type of iteration to be performed is the "shuttling back and forth" between the different shells which, within the present procedure, occurs when the simultaneous eigenvalue equations of Equation 1.22 are solved to determine the NO coefficients $C_{\mu i}$. But this part of the calculation was found to be an almost trivial phase of the total iteration scheme.

SEPARATED PAIR APPROXIMATION FOR BERYLLIUM-LIKE SYSTEMS

General Form of Geminals

Expansion in Slater-type atomic orbitals

The antisymmetrized product of separated geminals (APSG) for the ground state of the beryllium-like atoms is written as

$$\Phi = \mathcal{A}\{\Lambda_K(1,2)\theta_K(1,2)\Lambda_L(3,4)\theta_L(3,4)\}, \tag{1.38}$$

where Λ_K and Λ_L are geminals of S symmetry describing the K and L shells respectively and

$$\theta_K(i,j) = \theta_L(i,j) = \{\alpha(i)\beta(j) - \beta(i)\alpha(j)\}/\sqrt{2} \tag{1.39}$$

are singlet spin functions. Because of the S symmetry of the geminals, the natural orbitals (NO's) can be shown to belong to irreducible representations of the rotation group and it seems convenient to write the geminal expansion (Equation 1.4) in the form

$$\Lambda_\gamma(1,2) = \sum_{n\ell} C_{\gamma n\ell}\Lambda_{\gamma n\ell}(1,2) \tag{1.40}$$

with

$$\Lambda_{\gamma n\ell} = (2\ell+1)^{-\frac{1}{2}} \sum_m \phi_{\gamma n\ell m}(1)\phi_{\gamma n\ell m}^{*}(2), \quad (\gamma = K,L) \tag{1.41}$$

where

$$\phi_{\gamma n\ell m} = R_{\gamma n\ell m}(r)Y_{\ell m}(\theta,\phi) \tag{1.42}$$

are the natural orbitals of the geminal Λ_γ, $R_{\gamma n\ell m}$ being the radial part and $Y_{\ell m}$ being the spherical harmonic. The natural orbitals are constructed as linear combinations of Slater-type atomic orbitals (STAO's)

$$(n'\ell m\gamma) = (2\zeta)^{n'+\frac{1}{2}}[(2n')!]^{-\frac{1}{2}} r^{n'-1} e^{-\zeta r} Y_{\ell m}(\theta,\phi), \qquad (1.43)$$

where ζ is a function of n', ℓ and γ. The STAO's $(n'\ell m\gamma)$ are the main contributors to the geminal Λ_γ; however, the latter also contains small admixtures of other STAO's $(n'\ell m\gamma')$ because of orthogonality reasons. In the sequel the notation

$(\gamma n\ell) \equiv$ the set of the $(2\ell + 1)$ NO's $\phi_{\gamma n\ell m}$, $(m = -\ell, -\ell+1, \ldots +\ell)$

and

$(n'\ell\gamma) \equiv$ the set of the $(2\ell + 1)$ STAO's $(n'\ell m\gamma)$, $(m = -\ell, -\ell+1, \ldots +\ell)$

will also be used.

In practice the first step in the construction of the NO's is the Schmidt orthogonalization of all STAO's used in a given calculation. The resulting orthogonalized STAO's $\chi_1, \chi_2, \chi_3, \ldots$ then are taken to be the basis referred to in Equation 1.7. In the zeroth approximation, the matrix T is set equal to the unit matrix; the final value of T determines the actual form of the natural orbitals.

Transformation matrix T

For a given set of orthogonalized STAO's χ_i, the number of natural orbitals which can be generated may be equal to or less than the number of χ_i's. It is found that most effective use of the basis set is made if the number of NO's equals the number of orthogonalized STAO's, i.e., if T is taken to be square. The importance of including as many NO's as STAO's is illustrated in Figure 1. Two APSG's are considered: Φ_2 containing three K NO's and two L NO's and Φ_3 containing six K NO's and two L NO's. The NO's are expressed in terms of two basis sets, b_2 containing five basis functions and b_3 containing eight basis functions. The energy value calculated from Φ_2 using b_3 lies between that calculated from Φ_2 using b_2 and that from Φ_3 using b_3. The energy was minimized with respect to all parameters in these three cases. Thus, although the NO's are improved by taking a larger basis, the introduction of new NO's contributes a substantial energy lowering. That each NO gives a unique energy contribution will be discussed later with the analysis of the separated pair approximation. Henceforth T is taken to be square.

In the subsequent section it will be seen that in all cases T does not differ greatly from the unit matrix *if* the Schmidt orthogonalization is based on the following ordering of the original STAO's:

$$(1sK,2sL,2sK,3sK,3sL,4sK),(2pL,2pK,3pK,3pL,4pK),(3dK,3dL,4dK),(4fK). \tag{1.44}$$

Hence, the principal contribution to each of the NO's turns out to be one of the Schmidt orthogonalized STAO's χ_i. *In the following it therefore will be understood that* $(\gamma n\ell m)$ *denotes that NO which has as its principal component the orbital* $\chi = (n\ell m\gamma\perp)$, *which denotes the Schmidt orthogonalized STAO* $(n\ell m\gamma)$.

Nevertheless, it should be noted that the optimization of T is important, as can be seen from Figure 2. Comparison of the energies calculated using the Schmidt orthogonalized STAO's with the energies obtained with use of the best T for several separated pair approximations shows that the energy is improved by at least -0.015 a.u. Henceforth, the results reported are for optimized T.

Separated pair approximations to different degrees of accuracy

A systematic study of the effect of including various NO's and the corresponding STAO's from the List 1.44 in the beryllium separated pair approximation (Figure 3) shows that the energy lowering which results from the addition of a particular NO (and the corresponding STAO) is approximately constant, regardless of which other orbitals are present. In view of these results, various separated pair approximations can be constructed by including those and only those natural orbitals (and associated STAO's) which yield a certain degree of accuracy. Four such approximations for the beryllium atom are defined as the APSG's Φ_1, Φ_2, Φ_3 and Φ_4 in Figure 4. These four approximations were chosen in the systematic study of beryllium-like atoms.

Optimal Geminals

Natural orbitals

For the APSG's Φ_1, Φ_2 and Φ_3 the energy was minimized with respect to all three kinds of variations as discussed earlier. In the case of the APSG Φ_4 the occupation coefficients and the transformation matrix T were varied for fixed STAO exponents. The latter were taken from Φ_3 and estimated from assumed linear trends in the nuclear charge Z and in the quantum numbers n and ℓ. The STAO exponents determined in this way for Φ_1, Φ_2, Φ_3 and Φ_4 are listed in Figure 5. Polynomial approximations to the STAO exponents for Φ_1, Φ_2 and Φ_3 are given in Figure 6.

The scale factors

$$\eta = (-\frac{1}{2}\ \text{Potential Energy})/(\text{Kinetic Energy}) \qquad (1.45)$$

which indicate the deviations from the virial theorem are given in Figure 7. It may be noted that although the STAO exponents used in APSG Φ_4 were not varied, the deviations are no greater than those for the other APSG's. If all orbital exponents of a wavefunction are corrected by multiplication with the corresponding η, a better APSG which exactly satisfies the virial theorem is obtained. (Within the accuracy of the present calculations, the occupation coefficients and the T matrices remain unaffected by this scaling process because $(\eta-1)^2$ is less than the number of significant figures carried.) The strong linear dependence of the orbital exponents on Z permits the estimation of initial values for each new atomic calculation.

For the APSG's Φ_2, Φ_3 and Φ_4 the optimum transformations T (associated with the orbital exponents in Figure 5) are listed in Figures 8, 9 and 10, respectively. Corresponding elements T_{ij} from different atoms exhibit marked quantitative similarities, i.e., a weak dependence on the nuclear charge.

The cusp condition imposes one constraint for each natural orbital, whereby it removes one degree of freedom for each NO in the variational problem. However, because minimization of the total energy was of prime interest in this calculation, no attempt was made to satisfy this condition. Consequently, the cusp values obtained for the beryllium atom range from -3.7 for the (K1s) and (L2s) NO's to values quite different from -4 for NO's which occur with very small occupation coefficients.

Occupation coefficients

The occupation coefficients for beryllium-like atoms listed in Figure 11 show that the separated pair approximation consists mainly of (K1s), (L2s) and (L2p) NO's. The large contribution of the occupation coefficients of the (L2s) and (L2p) NO's can be accounted for by the degeneracy of the 2s and 2p atomic orbitals in the wavefunction of the zeroth-order perturbation theory. From the discussion of four-electron atoms by Linderberg and Shull (1960) it follows that for infinite nuclear charge the only non-zero occupation coefficients are $C_{K1s} = 1.0$, $C_{L2s} = +0.97432062$ and $C_{L2p} = -0.22516511$ and that the natural orbitals are the 1s, 2s and 2p hydrogenic atomic orbitals. It may also be noted that the occupation coefficients remain approximately constant as the separated pair approximation is improved and that those of the (K1s) and (L2s) NO's increase with an increase in the nuclear charge.

Within a separated geminal, the occupation numbers (i.e., the squares of the occupation coefficients) given in Figure 12 are not proportional to the energy lowering contributions reported in Figure 3. However, it is seen that the occupation numbers of the "new" NO's in the more accurate approximation Φ_i (i = 2,3,4) are consistently smaller by about an order of magnitude than the NO's which are already present in the less accurate approximation Φ_{i-1}. The choice of Φ_1, Φ_2, Φ_3 and Φ_4 as approximations to various degrees of accuracy is therefore essentially supported by the order of importance of the NO's deduced from the occupation numbers. The (K4s) NO seems to be an exception. It is of course not possible to compare the energy lowering contributions from different geminals by merely considering the occupation numbers because the values of the energy integrals are very different for the two shells.

Principal natural orbitals and Hartree-Fock approximation

Nazaroff and Hirschfelder (1963) have shown for two-electron systems that the antisymmetrized product (AP) formed with the first NO approximates the Hartree-Fock (HF) wavefunction to second-order perturbation theory and that the energy calculated from the AP of the first NO approximates the Hartree-Fock energy to fourth-order perturbation theory. It is generally surmised that a similar relationship exists for more general systems.

A comparison of the AP's formed from (K1s) and (L2s), the principal natural orbitals (PNO's) of the various separated pair approximations, with the Hartree-Fock wavefunction is embodied in Figure 13. By and large, the relative difference between E(PNO), the energy calculated from the PNO-AP's, and the Hartree-Fock energy E(HF) decreases when the PNO's are taken from the more accurate separated pair approximations and when the atom is uncharged. The absolute deviation from the Hartree-Fock energy increases slowly from beryllium to neon +6 and is also quite large for lithium -1. For Φ_4 the deviation from the Hartree-Fock energy is approximately 0.001 a.u. for all atoms except lithium -1 for which it is 0.004 a.u.

The overlap integral between the AP formed from the PNO's and the Hartree-Fock AP approaches unity when the PNO's are taken from more accurate separated pair approximations and as the nuclear charge increases. Consequently the PNO's span very nearly the same space as the HF orbitals and the question arises which of the possible SCF orbitals are closest to the principal natural orbitals of the separated pair approximation.

Although it is generally believed that the localized SCF orbitals would be close to the natural orbitals (Edmiston and Ruedenberg, 1963), it turns out that, in the beryllium-like systems, the canonical SCF orbitals are much closer to the PNO's. In all cases, the near-orthogonal transformation leading from the canonical SCF orbitals to the PNO's corresponds to a rotation angle of less than two degrees. In contrast, it was found by Edmiston (1963a) that the localized SCF orbitals for beryllium are related to the canonical SCF orbitals by an orthogonal transformation corresponding to a rotation of about six degrees and that an angle of five to seven degrees is found in all K-shells of second row atoms.

Energy

Correlation energy recovered

Figure 14 contains information on the energies calculated within the separated pair approximations represented by the APSG's Φ_1, Φ_2, Φ_3 and Φ_4. Given are (i) the deviations from the experimental energies

$$\Delta E(\text{APSG } \Phi_i) = E(\text{APSG } \Phi_i) - E(\text{exact}) \tag{1.46}$$

and (ii) the percentage of correlation energy recovered

$$100\{E(\text{APSG } \Phi_i) - E(\text{HF})\}/\{E(\text{exact}) - E(\text{HF})\}. \tag{1.47}$$

Figure 14 also contains an extrapolation for the best energy value possible in the separated pair approximation, denoted by $\Delta E(\text{SP})$, which is estimated by a procedure to be discussed in the next section.

The exact non-relativistic energy was obtained with the formula

$$E(\text{exact}) = E^{++} + I_1 + I_2 + E(\text{rel.})$$

where E^{++} is the non-relativistic energy for the helium-like ions, as calculated by Pekeris (1958); I_1 and I_2 are the first and second ionization potentials (Moore, 1949) corrected to infinite nuclear mass, and E(rel.) is the correction for the 2s relativistic effects obtained by taking the difference between the relativistic energy of the four- and the two-electron atoms given by Hartmann and Clementi (Table IV, 1964). However for the beryllium atom, their reported value -0.000165 a.u. was used.

In order to estimate the exact energies for lithium -1 and neon +6, use was made of the fact that the exact power expansion in Z^{-1} starts with the terms

$$E(Z) = -1.25Z^2 + 1.5592742Z + a_0 + a_1Z^{-1} + a_2Z^{-2} + a_3Z^{-3} + \ldots$$

(Linderberg and Shull, 1960). A least squares fit of a cubic equation in Z^{-1} to the difference $\{E(Z) + 1.25Z^2 - 1.5592742Z\}$ for the atoms beryllium to fluorine +5 yields

$$a_0 = -0.868132 \qquad a_2 = 0.557555$$
$$a_1 = -0.179684 \qquad a_3 = -1.677943.$$

The maximum deviation of this approximation from the fitted values is 0.00025 a.u., and this is presumably also the error in the reported values for lithium -1 and neon +6 which are obtained from this formula. The Hartree-Fock energies are those reported by Roothaan, Sachs and Weiss (1960).

The essential result, illustrated in Figure 14, is that the separated pair approximation consistently recovers about 90 per cent of the correlation energy in all systems (89 ± 0.8 per cent for Φ_4, 89 to 91 per cent for the extrapolated separated pair approximation Φ_{SP}). As a consequence the amount of correlation energy recovered

$$E(\text{APSG}\ \Phi_i) - E(\text{HF}) \qquad (1.48)$$

increases almost linearly with nuclear charge. This is surprising since the APSG Ansatz is general enough to yield the exact wavefunction for $Z^{-1} = 0$.

Comparison with other investigations

To date several quantitative investigations of the beryllium atom within the separated pair approximation have been reported. Allen and Shull (1962) estimated that the "separated pair projection" of Watson's configuration interaction wavefunction (Watson, 1960) would give 85.68 per cent of the correlation energy. Szász (1963a) obtained 69.7 per cent of the correlation energy by using a wavefunction which contained pair correlations without requiring strong orthogonality.

For beryllium-like atoms, Linderberg and Shull (1960) and Watson (1961) performed a calculation which can be considered as a separated pair approximation containing two configurations, $1s^2 2s^2$ and $1s^2 2p^2$. McWeeny and Sutcliffe (1963) also applied the separated pair approximation to beryllium-like atoms. The accuracy of their results is between that of APSG Φ_1 and APSG Φ_2 as reported in Figure 14.

The calculations of Tuan and Sinanoğlu (1964) and Geller, Taylor and Levine (1965), which embody Sinanoğlu's many-electron theory and are related to the separated pair concept, will be discussed in a subsequent section.

Correction for K-geminal defect

The well known r_{12} behavior of the K-shell cannot be described completely by a finite natural orbital expansion. By comparison with helium-like atoms, it can be expected that even for the separated pair approximation Φ_4 this type of deficiency may lead to an error of 0.002 a.u. in the energy. In order to arrive at an estimate of this error, let E(SP) be the energy of the exact separated pair approximation and E(APSG Φ_i) that of APSG Φ_i, so that

$$E(SP) = E(APSG\ \Phi_i) + D_i \qquad (1.49)$$

defines the difference D_i. If D_i arises from the K-shell only, it can be compared with the analogous error D_i^{++} obtained for the corresponding two-electron ion. Let E^{++} be the exact energy of that ion and E_i^{++} the energy obtained for it with the approximate wavefunction Φ_i^{++} <u>constructed from the same basis orbitals as</u> Φ_i so that D_i^{++} is defined by

$$E^{++} = E_i^{++} + D_i^{++}. \qquad (1.50)$$

One might expect D_i^{++} to be a minimum estimate for D_i, so that

$$D_i = D_i^{++} + \delta D_i \qquad (1.51)$$

where all three quantities are negative. If δD_i is small compared to D_i^{++} then D_i^{++} is a reasonable estimate for the defect D_i.

To obtain comparative separated geminal energies E(APSG Φ_i) and E_i^{++}, the calculations should contain the same number and symmetry types of K-geminal NO's in both systems. Because the accuracy of the NO's depends on the basis set chosen, it also is important for the determination of the NO's and occupation coefficients to choose comparable basis sets for each case. Two possible choices are conceivable: either (i) to use all the STAO's occurring in the four-electron wavefunction or (ii) to use only the K STAO's of the beryllium-like atoms. Further, the STAO exponents may be re-varied or taken directly from the four-electron atoms without change. For a given basis set the energy E_i^{++} then is minimized by optimizing the transformation T and the occupation coefficients. Fortunately there is no significant difference between the results obtained with the various assumptions. Thus, the energy values E_2^{++} obtained for several atoms with the use of the bases (i) and (ii) for fixed STAO exponents and with the basis (ii) for optimized STAO's are within 0.0004 a.u. of each other. This deviation is small compared to D_2^{++}. The results E_i^{++} and D_i^{++} are given in Figure 15. (E_3^{++} is calculated with basis (i); E_4^{++}, with basis (ii). The orbital exponents of the four-electron systems are used in both cases.) The values listed in Figure 14 for the extrapolated separated pair approximations are obtained from the energy estimate

$$E(SP) \approx E(APSG\ \Phi_4) + D_4^{++} \qquad (1.52)$$

Comparison with Calculations Based on Sinanoğlu's Theory

Very accurate calculations for beryllium have been made by Tuan and Sinanoğlu (1964), hereafter referred to as TS, and Geller, Taylor and

Levine (1965), hence referred to as GTL, who use Sinanoğlu's many-electron theory (Sinanoğlu, 1962a, 1962b). The following two factors are pertinent in order to relate their work to the present work. (i) Edmiston (1963b) has shown the following: Within the limitation to intrashell correlations Sinanoğlu's method represents "a single iteration, beyond SCF, in separated pair theory" including certain additional simplifications which imply that all electronic interactions between the changes of the geminals beyond the Hartree-Fock approximation are neglected. (ii) GTL have stressed that application of Sinanoğlu's scheme does not reduce the "many-electron problem to a set of two-electron problems". The difficulties encountered arise from the antisymmetrization of the wavefunction and are the usual ones, such as the presence of cluster integrals when interelectronic coordinates are used. The following remarks can therefore be made with regard to the similarities and differences between the investigations of TS and GTL and the present work.

1. In the present investigation a solution for the separated pair approximation is obtained by means of the variational principle applied to the total wavefunction. The investigations of TS and GTL represent a solution of the same problem by means of a perturbation calculation starting with the Hartree-Fock approximation. (The two-electron perturbation equations are solved variationally but the variational principle is not used for minimization of the total energy.) For the beryllium atom GTL obtain the total energy -14.659420 a.u. exclusive of intershell correlations which is in remarkable agreement with the present result of -14.65923 a.u. for Φ_{SP}. Unless second and higher order terms cancel

each other due to alternation in sign, the agreement indicates that the higher perturbations are negligible. Support for this conclusion is evident from the fact that interactions of the weakly occupied natural orbitals seem to be negligible, as will be shown by the analysis in the section on partitioning of energy. The complete neglect of these terms can, of course, also be incorporated without any difficulty in the present method of obtaining the separated pair approximation (if such neglect is known to be valid in advance). Whereas the variational method always furnishes an upper limit, this is not guaranteed within the perturbation approach when the higher order perturbations are no longer negligible.

2. In the present work the K-geminal is represented by a natural orbital expansion, but it is expressed with the help of interelectronic distances in the investigations of TS and GTL. (The latter also tested r_{34} for the L-shell but found it to be less effective than the orbital representation.) The NO expansion leads to a greater number of electron interaction integrals, but the use of r_{12} leads to more complex and more difficult integrals. In the current implementation and in that of GTL the time required to calculate one energy value appears to be comparable for the most complex wavefunctions. However, for molecules it would appear next to impossible to use interelectronic distances in the K-shell with the present knowledge of integral evaluations.

3. The investigations by TS and GTL are based on previous knowledge of an explicit SCF function. Since, in the work of GTL, the correlation correction to the wavefunction contains only one orbital exponent, minimization with respect to this non-linear parameter was not too time consuming.

In the present work all natural orbitals including the principal ones were determined ab initio. In view of the NO expansions of the K-shell, many non-linear parameters were minimized and this procedure was of course time consuming. Efficient use of minimization results from the simpler APSG's Φ_1, Φ_2 and Φ_3 was therefore essential in order to save computer time in the determination of APSG Φ_4. In future molecular applications one would start with rather accurate knowledge of NO expansions for the inner shells so that the corrective K-shell minimizations would presumably be rather trivial.

4. The figures in the previous sections exhibit the explicit wavefunction in a very simple form, viz., in terms of the natural orbitals. Neither TS nor GTL list the four-electron wavefunction which corresponds to their energy values. It appears likely that for other applications the separated pair approximation in natural orbital form would be an easier function to use. A very interesting question is how closely the total energy values obtained by TS or GTL would agree with the expectation values of the Hamiltonian operator calculated from their corresponding wavefunctions.

5. Both methods permit an analysis of the correlation energy and thus give insight into the origin of the energy lowering. A comparison of the two types of analyses will be discussed in the section on partitioning of energy. The present analysis which is somewhat more detailed, appears to suggest a possible improvement of Sinanoğlu's method in cases where several geminals have more than one strongly occupied orbital.

6. All previous remarks apply exclusively to the intrashell

correlation calculations of TS and GTL. Sinanoğlu's theory also predicts intershell correlation energies, and approximate values for these have been obtained by TS. These correlation effects cannot be obtained, of course, within the framework of the separated pair approximation. This matter will be taken up in Part II which deals with the addition of suitable configuration interaction terms to the separated pair approximation.

ENERGY ANALYSIS IN THE SEPARATED PAIR APPROXIMATION

General Partitioning and Correlation Energy

It is clearly of interest to understand how the separated pair approximation leads to a substantial energy lowering. To gain such insight an appropriate partitioning of the energy is indicated in the hope of finding major, minor and negligible contributions. Such an analysis would also illuminate the understanding of correlation energy since a major part of the latter is recovered by the separated pair approximation. It stands to reason that the desired partitioning would contain intrageminal and intergeminal contributions, and a further decomposition into natural orbital contributions appears likely. It is a straightforward matter to decompose the Energy Expression 1.12 into the form

$$E(SP) = E(PNO) + \Delta E \tag{1.53}$$

where

$$E(PNO) = \sum_{\mu} \mathcal{E}(\mu 0,\mu 0) + \sum_{\mu<\nu} \mathcal{J}(\mu 0,\nu 0) \tag{1.54}$$

is the energy of the antisymmetrized product (AP) built from the principal natural orbitals of each of the separated geminals. The definitions of $\mathcal{E}(\mu 0,\nu 0)$ and $\mathcal{J}(\mu 0,\nu 0)$ are those of Equations 1.14 and 1.16. Because in the previous discussion of the principal NO's it was found that E(PNO) very closely approximates the Hartree-Fock energy, the lowering ΔE defined by Equation 1.53 very nearly represents the correlation energy recovered in the separated pair approximation. *The following analysis of ΔE therefore essentially furnishes an understanding of the correlation energy recovered in the separated pair approximation.*

Subtracting Equation 1.54 for E(PNO) from Equation 1.12 for E immediately yields the following decomposition of ΔE into intrageminal and intergeminal correlation contributions

$$\Delta E = \sum_{\mu} \Delta E(\mu) + \sum_{\mu<\nu} \Delta I(\mu,\nu), \tag{1.55}$$

where

$$\Delta E(\mu) = E(\mu) - \mathcal{E}(\mu 0,\mu 0), \tag{1.56}$$

$$\Delta I(\mu,\nu) = I(\mu,\nu) - \mathcal{I}(\mu 0,\nu 0). \tag{1.57}$$

A further partitioning according to natural orbitals is obtained by substitution from Equations 1.14 and 1.16, namely,

$$\Delta E(\mu) = \sum_{i,j} \Delta\mathcal{E}(\mu i,\mu j), \tag{1.58}$$

$$\Delta I(\mu,\nu) = \sum_{i,j} \Delta\mathcal{I}(\mu i,\nu j) \tag{1.59}$$

where the following definitions are being introduced:

$$\Delta\mathcal{E}(\mu i,\mu i) = c_{\mu i}{}^2\{\mathcal{E}(\mu i,\mu i) - \mathcal{E}(\mu 0,\mu 0)\}, \tag{1.60}$$

$$\Delta\mathcal{E}(\mu i,\mu j) = c_{\mu i}c_{\mu j}\mathcal{E}(\mu i,\mu j) \quad (i \neq j) \tag{1.61}$$

and

$$\Delta\mathcal{I}(\mu i,\nu j) = c_{\mu i}{}^2 c_{\nu j}{}^2\{\mathcal{I}(\mu i,\nu j) - \mathcal{I}(\mu 0,\nu 0)\}. \tag{1.62}$$

In those cases where the separated pair approximation is effective, one would expect the *intrageminal* correlation contributions $\Delta E(\mu)$ to be *dominant*; and in the systems investigated here, they are indeed found to be the source of the energy lowering: they are negative and much larger than the intergeminal correlation contributions $\Delta I(\mu,\nu)$. Moreover, the latter are sometimes negative and sometimes positive. The intrageminal contributions $\Delta E(\mu)$ of Equation 1.58 contain two kinds of terms, the "off diagonal" terms $\Delta\mathcal{E}(\mu i,\mu j)$ $(i \neq j)$ and the "diagonal" terms $\Delta\mathcal{E}(\mu i,\mu i)$. The former are exchange energies; the dominant ones are negative and represent the essential source of the energy lowering furnished by $\Delta E(\mu)$. The latter must be considered as the "promotion energies" arising from that amount of charge occupying the orbitals (μi) for $i \neq 0$; they are positive and partially cancel the negative exchange energy. A crucial point of the following analysis is the observation that <u>for the weakly occupied NO's</u> this cancellation eliminates almost exactly one half of the exchange energy.

Quantitative insight into this matter is obtained by writing Equation 1.58 as follows:

$$\Delta E(\mu) = \sum_i \Delta\mathcal{E}(\mu i) \tag{1.63}$$

with

$$\Delta\mathcal{E}(\mu i) = \sum_j \Delta\mathcal{E}(\mu i,\mu j). \tag{1.64}$$

The $\Delta\mathcal{E}(\mu i)$ are orbital correlation contributions; the $\Delta\mathcal{E}(\mu i,\mu j)$ are orbital interactions. The observations just made correspond to the fact that only the strongly occupied natural orbitals contribute substantial contributions $\Delta\mathcal{E}(\mu i)$ and that the dominant ones, in particular $\Delta\mathcal{E}(\mu 0)$, are negative. Reasons for this can be seen in the following argument.

By multiplying the Eigenvalue Equation 1.22 with $C_{\mu i}$, by subtracting $C_{\mu i}C_{\mu j}\mathcal{E}(\mu 0,\mu 0)\delta_{ij}$ from both sides of the resulting equation and, finally, by substituting Equation 1.19 for $\mathcal{J}(\mu i)$, one finds the relation

$$\Delta\mathcal{E}(\mu i) = -C_{\mu i}^{2}\{\mathcal{E}(\mu 0,\mu 0) - \epsilon_{\mu} + \sum_{\nu(\neq\mu)} \mathcal{J}(\mu 0,\nu 0)$$

$$+ \sum_{\nu(\neq\mu)} \sum_{j} C_{\nu j}^{2}[\mathcal{J}(\mu i,\nu j) - \mathcal{J}(\mu 0,\nu 0)]\}. \qquad (1.65)$$

The double sum in the parenthesis will be small compared to the other terms because the differences $[\mathcal{J}(\mu i,\nu j) - \mathcal{J}(\mu 0,\nu 0)]$ are usually small; and moreover, only a few of the $C_{\nu j}^{2}$ are substantial, namely, those of the strongly occupied NO's. Consequently the total expression in braces depends only weakly upon the index i, and the approximate relations

$$\frac{\Delta\,\mathcal{E}(\mu i)}{\Delta\,\mathcal{E}(\mu j)} \approx \frac{C_{\mu i}^{2}}{C_{\mu j}^{2}} \qquad (1.66)$$

are found to be valid to within an order of magnitude. Hence the contributions from the strongly occupied NO's far outweigh the others in Equation 1.63.

Further insight into the orbital correlation contributions $\Delta\mathcal{E}(\mu i)$ of Equation 1.64 is obtained by writing

$$\Delta\mathcal{E}(\mu i) = \Delta\mathcal{E}(\mu i,\mu i) + \sum_{j(\neq i)} \Delta\mathcal{E}(\mu i,\mu j). \qquad (1.67)$$

Consider first the principal contributions $\Delta\mathcal{E}(\mu 0)$. By inserting Equations 1.60 and 1.61, one obtains

$$\Delta\mathcal{E}(\mu 0) = C_{\mu 0} \sum_{j(\neq 0)} C_{\mu j}\mathcal{E}(\mu 0,\mu j). \qquad (1.68)$$

According to Equation 1.14 the exchange integrals $\mathcal{E}(\mu 0,\mu j)$ $(j \neq 0)$ are all positive. Since $\Delta\mathcal{E}(\mu 0)$ is the largest negative orbital correlation contribution to $\Delta E(\mu)$ in Equation 1.63, it follows that the more important coefficients $C_{\mu j}$ must be negative if $C_{\mu 0}$ is chosen to be positive.

Consider next contributions $\Delta\mathcal{E}(\mu i)$ for $i \neq 0$ arising from secondary natural orbitals which, though not principal NO's, are still strongly occupied. First it is to be noted that $\Delta\mathcal{E}(\mu i,\mu i)$ is positive since, according to Equation 1.60, it represents the energy required to promote the fraction $C_{\mu i}^{2}$ of an electron from the lower orbital $(\mu 0)$ to the higher orbital (μi). (This is mostly a kinetic energy effect.) On the other hand, the orbital interaction $\Delta\mathcal{E}(\mu 0,\mu i)$ is negative because it is the same one which appeared in $\Delta\mathcal{E}(\mu 0)$. A partial cancellation between $\Delta\mathcal{E}(\mu i,\mu i)$ and $\Delta\mathcal{E}(\mu 0,\mu i)$ occurs. The remaining terms are much smaller. The result $\Delta\mathcal{E}(\mu i)$ is negative but, smaller than $\Delta\mathcal{E}(\mu 0)$.

Finally consider $\Delta\mathcal{E}(\mu i)$ for the weak orbital correlation contributions. Again $\Delta\mathcal{E}(\mu i,\mu i)$ is positive as before. But the argument leading to Equation 1.65 showed that $\Delta\mathcal{E}(\mu i)$ is very small; so that, there is now a nearly complete cancellation by the terms $\Delta\mathcal{E}(\mu i,\mu j)$ for $j \neq i$. In this case the promotion energy for orbital (μi) is almost exactly balanced by one half of the sum over all orbital interactions with (μi), viz.,

$$\Delta\mathcal{E}(\mu i,\mu i) \approx \sum_{j(\neq i)} \Delta\mathcal{E}(\mu i,\mu j). \tag{1.69}$$

The largest of these are the $\Delta\mathcal{E}(\mu i,\mu 0)$; and they can, therefore, be expected to be negative.

These considerations lead one to anticipate that the coefficients $C_{\mu j}$ for $j \neq 0$ are negative for major as well as for minor admixtures; i.e., they lead to the following general conjecture: _If the principal natural orbital coefficients are chosen positive, then all other natural orbitals have negative coefficients, provided that the separated pair_ approximation is effective. All cases considered in this investigation, as well as the results for the helium atom reported by Shull and Löwdin (1959) and those for the hydrogen molecule reported by Davidson and Jones (1962), substantiate this conjecture. On the other hand, the determinations of the natural orbitals for the hydrogen molecule by Hagstrom and Shull (1959) and for the He_2^{++} ion by Shull and Prosser (1964) did yield a few very weakly occupied natural orbitals with positive occupation coefficients. In view of Davidson and Jones's work, this may be a spurious result which could have arisen from numerical truncation errors.

Quantitative Discussion of Beryllium-like Systems

In the beryllium-like systems Equation 1.55 becomes

$$\Delta E = \Delta E(K) + \Delta E(L) + \Delta I(K,L). \tag{1.70}$$

Moreover the K-geminal has only one strongly occupied NO, namely, the principal one (K1s); all other (Ki)'s are very weakly occupied. The L-geminal has two strongly occupied NO's: the principal one, (L2s) with occupation number 0.9; and the secondary one, (L2p) with occupation number 0.1. One finds that almost all the energy lowerings are accounted for by the leading terms

$$\Delta E(K) \approx \Delta\mathcal{E}(K1s), \tag{1.71}$$

$$\Delta E(L) \approx \Delta\mathcal{E}(L2s) + \Delta\mathcal{E}(L2p), \tag{1.72}$$

$$\Delta I(K,L) \approx \Delta\mathcal{I}(K1s,L2p). \tag{1.73}$$

The remaining terms of Equations 1.59 and 1.63 contribute virtually nothing. (In beryllium they contribute 0.00005 a.u. to a ΔE of 0.08554 a.u.)

According to Equation 1.64, the three orbital correlation contributions on the right hand side of Equations 1.71 and 1.72 are sums of interactions with all other natural orbitals. This resolution of $\Delta\mathcal{E}(K1s)$, $\Delta\mathcal{E}(L2s)$ and $\Delta\mathcal{E}(L2p)$ in terms of orbital interactions is illustrated in Graph 1 for the case of the APSG Φ_4 of beryllium. Qualitatively identical graphs are obtained for the other systems.

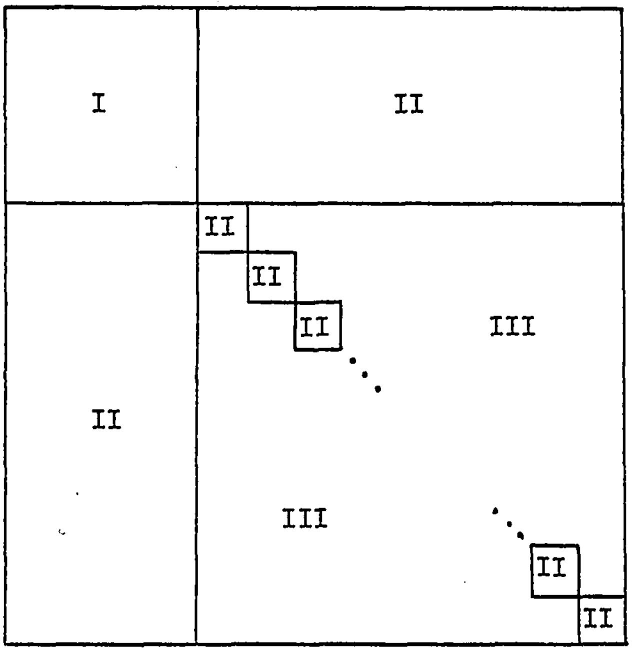
The exact quantitative breakdown of the energies is exhibited in Figures 16 through 23 for the wavefunctions Φ_2, Φ_3 and Φ_4, respectively. These data substantiate the main points just made and furnish many interesting insights into the correlation energy. Particularly remarkable is the fact that, for any given atom, the individual orbital contributions $\Delta\mathcal{E}(K1s,Ki)$, $\Delta\mathcal{E}(L2s,Lj)$, $\Delta\mathcal{E}(L2p,Lj)$ and $\Delta\mathcal{E}(K1s,L2p)$ have very nearly the same value for the APSG's Φ_2, Φ_3 and Φ_4.

A graphical representation of the dependence of the various energy contributions on Z for Φ_4 is given in Graph 2. All energy contributions show a near-linear dependence on Z. This dependence is very weak for the total K-shell lowering $\Delta E(K)$ and for all its components $\Delta\mathcal{E}(Ki,Kj)$, but they are not as constant as in the helium-like systems. The dependence on Z is strong for the total L-shell lowering $\Delta E(L)$ and all its components $\Delta\mathcal{E}(Li,Lj)$. It is noteworthy that the intergeminal interaction $\Delta I(K,L)$, too, exhibits a strong linear dependence on Z, a correlation which shows the negative value of this quantity in lithium -1 to be consistent with the positive values in all other atoms. The total energy lowering E(APSG Φ_4) - E(PNO) has a slope (-0.0122) almost identical with the theoretical slope (-0.01173) of the correlation energy (E(exact) - E(HF)). This fact seems to imply that APSG Φ_4 is general enough to recover that portion of the energy which depends linearly on Z.

On the basis of the present analysis it finally becomes possible to understand better the results obtained for the "improvement" due to certain natural orbitals which were reported earlier in Figure 3. For example, in Figure 17 the contribution for beryllium from APSG Φ_4 for the (K4f) NO is $\Delta\mathcal{E}(K1s,K4f) = -0.00061$ a.u.; for the (L2p) NO the contributions are $2\Delta\mathcal{E}(L2s,L2p) + \Delta\mathcal{E}(L2p,L2p) + \Delta\mathcal{E}(K1s,L2p) = -0.04426$ a.u.; for the (L3d) NO they are $\Delta\mathcal{E}(L2s,L3d) + \Delta\mathcal{E}(L2p,L3d) = -0.00043$ a.u. etc. These numbers agree very closely with the corresponding ones in Figure 3. The agreement between the two methods of assessing the energy contributions for each NO and the unique character of the energy contributions for each NO in the energy partitioning suggest that a separated pair approximation using as many NO's as possible may be chosen arbitrarily and then analyzed to determine the importance of each NO.

Secondary Natural Orbitals, Dynamical and Non-dynamical Correlation

Suppose that a geminal has several secondary natural orbitals (SNO's), then the matrix of orbital interactions, whose sum appears on the right hand side of Equation 1.58, can be divided into three groups of elements according to their relative importance in the following way:



Block I contains the interactions between the principal NO and the secondary NO's and those between the latter, i.e., the terms

$$\Delta E^{st}(\mu) = \sum_{i}^{st}\sum_{k}^{st}\Delta\mathcal{E}(\mu i,\mu k)$$

where Σ^{st} indicates a sum over the strongly occupied NO's only. The elements in the areas indicated by II are the interactions of the strongly occupied NO's and the weakly occupied NO's plus the promotion energies of the latter. Their sum is

$$\Delta E^{sw}(\mu) = \sum_{i}^{wk}\{\Delta\mathcal{E}(\mu i,\mu i) + 2\sum_{k}^{st}\Delta\mathcal{E}(\mu i,\mu k)\} \approx \sum_{k}^{st}\sum_{i}^{wk}\Delta\mathcal{E}(\mu i,\mu k) \qquad (1.74)$$

where Σ^{wk} indicates summation over the weakly occupied NO's. The elements in area III, finally, being interactions of weakly occupied NO's only, are negligible so that

$$\Delta E(\mu) \approx \Delta E^{st}(\mu) + \Delta E^{sw}(\mu). \tag{1.75}$$

This decomposition of $\Delta E(\mu)$ is analogous to the decomposition of the correlation energy into a "dynamical" and a "non-dynamical" part (Tuan and Sinanoğlu, 1964); ΔE^{sw} represents the dynamical part of ΔE, and ΔE^{st} represents the non-dynamical part. The latter occurs only if secondary orbitals are present because $\Delta\mathcal{E}(\mu 0,\mu 0) = 0$.

Furthermore, from the example of beryllium, it can be seen that only the interactions of the strongly occupied NO's contribute to the right hand side of Equation 1.59

$$\Delta I(\mu,\nu) \approx \Delta I^{st}(\mu,\nu) = \sum_i^{st}\sum_j^{st}\Delta\mathcal{I}(\mu i,\nu j); \tag{1.76}$$

i.e., the intershell interactions are essentially non-dynamical. Because $\Delta\mathcal{I}(\mu 0,\nu 0) = 0$, they too arise only if secondary NO's are present. One can partition the intergeminal contribution $\Delta I(\mu,\nu)$ as follows:

$$\Delta I(\mu,\nu) = \Delta_{\mu} I(\mu,\nu) + \Delta I_{\nu}(\mu,\nu) + \Delta\tilde{I}(\mu,\nu), \tag{1.77}$$

$$\Delta_{\mu} I(\mu,\nu) = \sum_{i(\neq 0)} \Delta\mathcal{I}(\mu i,\nu 0) \approx \sum_i^{sec}\Delta\mathcal{I}(\mu i,\nu 0), \tag{1.78}$$

$$\Delta_{\nu} I(\mu,\nu) = \sum_{j(\neq 0)} \Delta\mathcal{I}(\mu 0,\nu j) \approx \sum_j^{sec}\Delta\mathcal{I}(\mu 0,\nu j), \tag{1.79}$$

$$\Delta\tilde{I}(\mu,\nu) = \sum_{i(\neq 0)} \sum_{j(\neq 0)} \Delta\mathcal{I}(\mu i,\nu j) \approx \sum_i^{sec}\sum_j^{sec}\Delta\mathcal{I}(\mu i,\nu j) \tag{1.80}$$

where Σ^{sec} indicates summation over secondary orbitals only. One can now argue that $\Delta_{\mu} I(\mu,\nu)$ contains interactions which are generated only by correlations occurring in the μ-geminal, that $\Delta_{\nu} I(\mu,\nu)$ contains interactions which are generated only by correlations in the ν-geminal and that, therefore,

$$\Delta\tilde{E}(\mu) = \Delta E(\mu) + \sum_{\nu(\neq\mu)} \Delta_{\mu} I(\mu,\nu) \tag{1.81}$$

could be considered as the total correlation contributions of geminal μ in the context of the total system. With this philosophy the energy decomposition given by Equation 1.55 can then be rewritten as

$$\Delta E = \sum_{\mu}\Delta\tilde{E}(\mu) + \sum_{\mu<\nu} \Delta\tilde{I}(\mu,\nu). \tag{1.82}$$

In the case of beryllium this would mean rearranging Equations 1.70 to 1.73 in the form

$$\Delta E = \Delta\tilde{E}(K) + \Delta\tilde{E}(L) + \Delta\tilde{I}(K,L), \tag{1.83}$$

$$\Delta\tilde{E}(K) = \Delta E(K) + \Delta_{K}I(K,L) \approx \Delta E^{sw}(K) \approx \Delta\mathcal{E}(K1s), \tag{1.84}$$

$$\Delta\tilde{E}(L) = \Delta E(L) + \Delta_{L}I(K,L) \approx \Delta E^{sw}(L) + \Delta E^{st}(L) + \Delta\mathcal{A}(K1s,L2p), \tag{1.85}$$

$$\Delta E^{st}(L) = \Delta\mathcal{E}(L2p,L2p) + 2\Delta\mathcal{E}(L2s,L2p), \tag{1.86}$$

$$\Delta E^{sw}(L) = \Delta\mathcal{E}(L2s) + \Delta\mathcal{E}(L2p) - \Delta E^{st}(L), \tag{1.87}$$

$$\Delta\tilde{I}(K,L) \approx 0. \tag{1.88}$$

The L-shell correlation energy usually quoted for beryllium corresponds essentially to the definition in Equation 1.85.

The foregoing analysis shows, however, that the weak interactions $\Delta\tilde{I}(K,L)$ do not find a logical place in this type of decomposition. Moreover, in general, there may occur additional non-negligible intergeminal terms $\Delta\tilde{I}(\mu,\nu)$ between secondary NO's of different geminals; and if this happens, the advantage of defining the $\Delta\tilde{E}(\mu)$ becomes questionable. At any rate it must be realized that, even in the separated pair approximation, there exist intergeminal interactions, usually of unfavorable type, which are engendered by the intra-orbital correlations. It may also be mentioned that, when non-negligible interactions $\Delta\tilde{I}(\mu,\nu)$ occur and are strong enough, they would have to be incorporated in Sinanoğlu's treatment where they are omitted presently.

Comparison with Other Methods of Analysis

A crucial point of the foregoing analysis is the specific grouping of terms adopted in Equations 1.63 and 1.64 because it leads to the result that most of the quantities $\Delta\mathcal{E}(\mu i)$ are negligible, as explained by Equation 1.65. It is in this respect that the present approach differs from an analysis given recently by Ebbing and Henderson (1965) in their work on lithium hydride. These authors essentially use an expression like Equation 1.58 without any further grouping of terms. An analysis of Ebbing and Henderson's separated pair approximation of lithium hydride according to the present scheme is given in Figure 24. The general pattern is in agreement with the preceding discussion. The inner geminal (I) is a K-geminal; the outer geminal (O) is the bonding geminal. There are two secondary NO's in the outer geminal, but neither is as important as the (L2p) NO in beryllium. Remarkable is the fact that $\Delta\mathcal{E}(O\chi 3)$ is positive (the promotion energy is larger than the exchange terms); it will be of interest to see whether this remains true in a more accurate calculation.

Kutzelnigg (1963a, 1963b and 1964) has given an approximate expression for the energy lowering ΔE. In the present notation it can be written

$$\Delta E(\text{Kutzelnigg}) \approx \sum_{\mu} \sum_{i(\neq 0)} (C_{\mu i}/C_{\mu 0})\mathcal{E}(\mu i,\mu 0). \qquad (1.89)$$

This equation is derived under the assumption that every geminal has, in addition to the principal NO, only weakly occupied NO's but no moderately occupied secondary NO's. In this case one can write $C_{\mu 0} = 1 - x_{\mu 0}$ with $x_{\mu 0} \ll 1$, so that $C_{\mu 0}^{-1} \approx C_{\mu 0} + 2x_{\mu 0}$; hence

$$\Delta E(\text{Kutzelnigg}) \approx \sum_{\mu} \Delta\mathcal{E}(\mu 0) \qquad (1.90)$$

which is indeed a good approximation in this special case. However, if there are secondary NO's such as in the beryllium L-geminal, there appear not only additional <u>intra</u>geminal terms but also <u>inter</u>geminal terms as discussed in the preceding section. Another insight into the Approximate Relation 1.90 is obtained by considering a two-electron case, such as helium, which has only a K-geminal. It can be shown exactly that

$$\Delta E = \Delta E(\text{Kutzelnigg}) = \Delta\mathcal{E}(K0) + (1 - C_{K0}^{2})\Delta E. \qquad (1.91)$$

The last term is negligible if all NO's except the principal ones are weak.

Finally, it is of interest to compare the present partitioning of the energy with partitionings based on perturbation treatments. There are three calculations of comparable accuracy, namely, that of Kelly (1963, 1964) who uses the Brueckner-Goldstone perturbation theory and those of Tuan and Sinanoğlu (1964) and of Geller, Taylor and Levine (1965) who use Sinanoğlu's many-electron theory. A comparison and critical summary of various calculations are given in Table V of GTL. Close agreement with the present work is obtained if one compares their correlation energies $E_{corr.}(1s^2)$, $E_{corr.}(2s^2)$ with $\Delta\tilde{E}(K)$ and $\Delta\tilde{E}(L)$ respectively, as discussed in the preceding section. The comparison is made in Figure 25.

INTERELECTRONIC COORDINATES IN THE PAIR APPROXIMATION FOR BERYLLIUM

Object and Scope

The success of introducing interelectronic coordinates into helium-like systems (Hylleraas, 1929; Pekeris, 1958, 1959; Kinoshita, 1957, 1959; Roothaan and Weiss, 1960; Kolos and Roothaan, 1960) has led many investigators to include pair correlations in beryllium-like systems by introducing interelectronic coordinates. Szász has formulated the mathematics of certain wavefunctions of this type and has applied this method to beryllium.

Such wavefunctions transcend the separated pair approximation even if the r_{ij} terms are introduced only for intrashell correlations, because geminals containing interelectronic coordinates violate the strong orthogonality condition. It was therefore considered to be of interest to test the importance of the additional freedom introduced by such terms and to investigate wavefunctions of the form

$$\tilde{\Phi} = a_0 \Phi + X \tag{1.92}$$

where Φ is the separated pair approximation and X is a correction of the type

$$\mathcal{A}\{K(1,2)\theta_K(1,2)L(3,4)\theta_L(3,4)f(r_{12},r_{34})\}. \tag{1.93}$$

If $f(r_{12},r_{34})$ is a product $g(r_{12})\cdot h(r_{34})-1$, then the Ansatz $\tilde{\Phi}$ would classify as an antisymmetrized product of geminals (APG).

In order to keep the problem tractable, the following simple form was assumed for the correction function:

$$X = a_K X_K + a_L X_L, \tag{1.94}$$

$$X_K = N_K \mathcal{A}\{\tilde{K}(1,2) r_{12} \theta_K(1,2) \tilde{L}(3,4) \theta_L(3,4)\}, \tag{1.95}$$

$$X_L = N_L \mathcal{A}\{\tilde{K}(1,2) \theta_K(1,2) \tilde{L}(3,4) r_{34} \theta_L(3,4)\} \tag{1.96}$$

where N_K and N_L are normalization constants and

$$\tilde{K}(1,2) = [1sK(1)][1sK(2)], \tag{1.97}$$

$$\tilde{L}(3,4) = [2sL(3)][2sL(4)] \tag{1.98}$$

are products of the principal STAO's of the K- and L-geminals. It is believed that the results would not be very different if one would use the separated geminals K(1,2) and L(3,4) for $\tilde{K}$ and $\tilde{L}$. Perhaps inclusion of the (L2p) NO (or in the above approximation the (2pL) STAO) in $\tilde{L}$ would have some effect; but most likely, it would be no larger than 4.4 per cent of the (L2s) contribution, which is the contribution of this NO to the L-geminal energy of the separated pair approximation.

However for a given choice of Φ, three calculations were made. In the first, the orbital exponents in $\tilde{K}$ and $\tilde{L}$ were taken to be those of the separated pair approximation. In the second, the orbital exponents in $\tilde{K}$ and $\tilde{L}$ were optimized. In the third, the occupation coefficients in Φ were also readjusted.

It is also believed that similar results would be obtained if in Equation 1.93 one would put

$$f(r_{12}, r_{34}) = (1 + a_K r_{12})(1 + a_L r_{34}). \tag{1.99}$$

That is, the cross term would be expected to have little influence; and hence, the present results will shed at least some light on the limitations imposed by the strong orthogonality constraint.

Method

For the separated pair approximation Φ_1, two wavefunctions of the type

$$\tilde{\Phi}_1 = a_{01}\Phi_1 + a_{K1}X_{K1} + a_{L1}X_{L1} \qquad (1.100)$$

were investigated: (1) with the orbital exponents in X_K and X_L equal to those in Φ_1; (2) with the orbital exponents in X_K and X_L reminimized. For the separated pair approximation Φ_2, three wavefunctions

$$\tilde{\Phi}_2 = a_{02}\Phi_2 + a_{K2}X_{K2} + a_{L2}X_{L2} \qquad (1.101)$$

were investigated. In addition to the two mentioned for Φ_1, a third was found by reminimizing also the occupation coefficients in Φ_2.

In all cases there results a three by three secular equation of the type

$$\sum_j (H_{ij} - \lambda S_{ij}) a_j = 0. \qquad (1.102)$$

The matrix elements consist of very complex integrals involving r_{ij} terms. Techniques for solving such integrals have been proposed by Szász (1961), Bonham (1965) and Öhrn and Nordling (1963). In the present calculation, the method of the last mentioned authors was used. The amount of algebraic formalism and manipulation as well as computer programming required for this part of the work was more laborious and time consuming by an order of magnitude than that needed for the investigation of separated pair approximations. It is much easier to add three basis orbitals to APSG Φ_2 and seven basis orbitals to APSG Φ_3 than to include r_{ij}-dependent terms in APSG Φ_1 or APSG Φ_2.

Thus, the amount of work as well as computer time and storage needed for carrying out similar calculations for Φ_3 and Φ_4 would have been so staggering that it was not considered a worthwhile investment.

Results

The wavefunctions and energies obtained in this way are listed in Figure 26. For calculation three, the modified occupation coefficients are

$$\begin{aligned} C_{K1s} &= 0.99962 & C_{L2s} &= 0.94155 \\ C_{K2s} &= -0.02136 & C_{L2p} &= -0.19449. \\ C_{K2p} &= -0.01001 & & \end{aligned} \tag{1.103}$$

The trends in energy improvement show that the energy calculated with APSG Φ_{i+1} is better than that calculated with APG $\tilde{\Phi}_i$ which contains interelectronic coordinates. This suggests that it is more advantageous to refine a separated pair approximation by adding more natural orbitals than by including interelectronic coordinates since (i) the computation time needed to calculate E(APG $\tilde{\Phi}_1$) is six times that needed to calculate E(APSG Φ_{i+1}) for $i = 1$ and 2; and (ii) if either the APG or the APSG is used as first term in a wavefunction which is being further improved to include <u>inter</u>geminal correlations, then the difference in ease of manipulation will be even more pronounced.

On the basis of the present results it is of course not possible to draw completely cogent conclusions regarding the difference between the pair approximation and the separated pair approximation. However, if $\tilde{\Phi}_2$ of Equation 1.101 is a reasonable approximation to the pair approximation without the strong orthogonality constraint, then the energy improvement E(APG $\tilde{\Phi}_2$) - E(APSG Φ_2) is an approximate measure of the effect of relieving this constraint in Φ_2. Better estimates would be obtained, of course, by carrying out the analogous calculations for Φ_3 and Φ_4.

A calculation of the beryllium ground state in the pair approximation without strong orthogonality restrictions has also been made by Szász (1963a) who used a wavefuntion containing powers of r_1, r_2, r_{12} and r_{34}. Rather surprisingly this calculation recovers only 73.6 per cent of the intrashell correlation energy which is not even as good as that obtained with APSG Φ_2. In light of the present investigation, the only deficiency of Szász's wavefunction is the absence of even powers of r_{12} and r_{34} which correspond to $(n\ell)^2$ terms in the natural geminal expansions. However for the K-shell, r_{12} would be expected to be just as effective; and, for the L-shell, the substitution of r_{34} for $(L2p)^2$ would not be expected to worsen the results by 15 per cent. See the calculations of Geller, Taylor and Levine (1965). The only explanation seems to be that the handling of r_{ij}-dependent terms is so complex and time consuming that exhaustive minimization with extensive expansions has not yet been achieved.

In spite of the incomplete evidence, the present investigation suggests that rather than to improve the separated pair approximation to the pair approximation, it may be wiser and more effective to include sufficient basis functions in the separated pair approximation and then recover the remaining correlations via the augmented separated pair expansion which is discussed in Part II.

PART II. AUGMENTED SEPARATED PAIR EXPANSION

INTRODUCTION

Although in many atomic and molecular systems the separated pair approximation represents a great improvement over the Hartree-Fock approximation, its total energy still appears to fall slightly short of chemical accuracy, and it may be necessary in certain cases to look for ways of further improving the electronic wavefunctions. In the beryllium atom, for example, the separated pair approximation recovers about 90 per cent of the correlation energy leaving an error of about 0.008 a.u. or 5 kcal. While the shortcomings of the separated pair approximation are usually attributed to two deficiencies, viz., the limitations arising from the strong orthogonality conditions and the failure to take into account correlation between different geminals, it is quite possible that these two inadequacies are not substantially different in nature. So far, no practical attempt has been made to improve the separated pair approximation consistently.

Even though the separated pair approximation may not lead to results within chemical accuracy, there can be little doubt that it is excellently suited as zeroth-order approximation for a more exact calculation. The advantage of the separated pair approximation over the Hartree-Fock approximation is not only that it is much closer to the true solution but, moreover, that it generates a set of natural orbitals which are close to the true natural orbitals of the problem. Since the latter are known to lead to the most rapidly converging configuration interaction expansion (Löwdin, 1955), the natural orbitals of the separated pair approximation can be expected to be highly appropriate for constructing additional configurations which effectively augment the separated pair approximation. This approach has the additional advantage that the refinement does not require any new basis integrals beyond those which occur already in the separated pair approximation itself.

The only extensive previous configuration interaction calculations which have made use of the variational principal are those for the beryllium-like atoms by Watson (1960) and by Weiss (1961). Watson's calculation indicates some of the configurations which recover correlations beyond the separated pair approximation. The calculation by Weiss, on the other hand, is rather awkward to analyze since it is based on configurations formed from non-orthogonal basis orbitals. The calculations of intershell correlation energy by Sinanoğlu (1962a, 1962b) and by Kelly (1963, 1964) do approximate the energy lowering beyond the separated pair approximation, but with perturbation theory taking the Hartree-Fock solution as a zeroth-order wavefunction. The consideration of possible configuration interaction wavefunctions by Kapuy (1960c, 1961a) built from two- as well as many-electron group functions does not include all possible configurations, because geminals in different configurations are postulated to be one-electron orthogonal. It appears doubtful whether this would be effective, even if Kapuy's complex formalism could be executed.

In the present investigation a refinement of the separated pair approximation is developed, in which the wavefunction is represented as an "augmented separated pair expansion"

$$\Psi = c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + \dots$$

where each term ψ_k is an antisymmetrized product of separated space geminals and spin eigenfunctions. The "separated pair configuration" ψ_0 is identical with the separated pair approximation; the "augmented separated pair configurations" $\psi_k (k \geq 1)$ are formed, according to certain simple rules, from the natural orbitals of the separated pair approximation. In the course of applying this approach to the beryllium-like atomic systems, straightforward criteria are found for identifying those relatively few augmented separated pair configurations which are effective in recovering most of the intershell correlation energy.

In this way, 96 per cent of the total correlation energy was recovered, equivalent to an accuracy of about 3 kcal in beryllium. The calculations were limited by the constraints of the computer used, an IBM 7074 with a 20,000 word core memory and no provision for double precision in Fortran. It is believed that under somewhat more favorable computational conditions and with somewhat more experience 98 to 99 per cent of the correlation may be recovered with a relatively compact wavefunction built from appropriate atomic orbitals.

GLOSSARY

Although all abbreviations are defined in the text, the following list may be helpful.

AP	antisymmetrized product
APSG	antisymmetrized product of separated geminals
SPA	separated pair approximation
Φ_{SP}	wavefunction corresponding to the exact separated pair approximation
Φ_i, APSG Φ_i	the i-th approximation to Φ_{SP}
SPC	separated pair configuration; identical with SPA in the context of the augmented separated pair expansion
ASPC	augmented separated pair configuration
ASPE	augmented separated pair expansion; an expansion containing the SPC and several ASPC's
Ψ_i, ASPE Ψ_i	the i-th approximation to the exact ASPE
AP-SH-G	antisymmetric product of a spin harmonic and geminals
AP-SH-SG	antisymmetric product of a spin harmonic and separated geminals

WAVEFUNCTION AND ENERGY IN THE AUGMENTED SEPARATED PAIR EXPANSION

Expansion in Spin Harmonics and Geminal Products

Expansion in terms of spin functions

If the Hamiltonian of an N-electron system commutes with the total spin, then the wavefunction can be written as a sum

$$\Psi = \sum_{\alpha=0}^{D-1} \psi_\alpha \tag{2.1}$$

with

$$\psi_\alpha = \bar{\mathcal{A}}(\theta_\alpha F_\alpha) \tag{2.2}$$

where the

$$\theta_\alpha(1,2,\ldots N) \text{ for } \alpha = 0,1,\ldots D-1 \tag{2.3}$$

with

$$D = \left(\frac{2S+1}{N+1}\right)\binom{N+1}{\frac{1}{2}N-S} \tag{2.3'}$$

are D pure spin functions and eigenfunctions of $\mathcal{S}^2$ and $\mathcal{S}$ with eigenvalues $\frac{1}{4}\hbar^2 S(S+1)$ and $(\frac{1}{2}\hbar m_s)$ respectively. The functions $F_\alpha(1,2,\ldots N)$ are pure space functions, and $\bar{\mathcal{A}}$ is the total antisymmetrizer of N-electrons.

The D spin functions can be constructed by the branching diagram method and form a basis for the irreducible representation D_S^N of the permutation group S_N; so that for any permutation, one has

$$P\theta_\beta = \sum_\alpha \theta_\alpha T_{\alpha\beta}(P), \tag{2.4}$$

and the $T_{\alpha\beta}$ can be obtained as the matrix elements

$$T_{\alpha\beta}(P) = (\theta_\alpha|P|\theta_\beta). \qquad (2.5)$$

Thus the functions ψ_α can also be written

$$\psi_\alpha = D^{-\frac{1}{2}}\sum_\beta \theta_\beta f_{\beta\alpha}, \qquad (2.6)$$

$$f_{\beta\alpha} = (D/N!)^{\frac{1}{2}}\sum_P(-1)^P T_{\beta\alpha}(P)(PF_\alpha), \qquad (2.7)$$

from which it can be seen that the set $(f_{1\alpha}, f_{2\alpha}, \ldots f_{D\alpha})$ forms a basis which transforms according to the representation which is conjugate to D_S^N.

The D functions $\bar{\mathcal{A}}(\theta_\alpha F)$, which can be constructed from <u>one</u> space function F, are linearly independent if the N! functions (PF) are linearly independent. On the other hand, the D functions $\bar{\mathcal{A}}(\theta_\alpha F')$ which are generated from the space function $F' = P_0F$, where P_0 is an arbitrary permutation, span exactly the same linear space as the D functions $\bar{\mathcal{A}}(\theta_\alpha F)$; i.e., use of (P_0F) instead of F as "primitive function" gives nothing new. The previous discussion is developed more thoroughly by Kotani *et al.* (1955).

Reduction with respect to geminal subgroups

An important simplification can be achieved by considering that particular subgroup Σ_R of the total permutation group S_N, which consists of the R simple interchanges

$$(12),(34),(56),\ldots(2R-1,2R) \qquad (2.8)$$

and all products between them. This is an abelian group of order 2^R which is the direct product of the R subgroups

$$\{e,(12)\},\{e,(34)\},\ldots\{e,(2R-1,R)\}. \qquad (2.9)$$

Each of these subgroups of order two has two irreducible one-dimensional representations, the symmetric one $\{1,1\}$ and the antisymmetric one $\{1,-1\}$. The direct product of these two possibilities for each of the R subgroups yields the 2^R irreducible representations of the group Σ_R. Each of these can therefore be characterized by a symbol such as $(\mathcal{E}_1,\mathcal{E}_2,\ldots\mathcal{E}_R)$, where $\mathcal{E}_\nu = (+)$ or $\mathcal{E}_\nu = (-)$ indicates that the subgroup $\{e,(2\nu-1,2\nu)\}$ belongs to the symmetric or antisymmetric representation respectively. All representations of Σ_R are one-dimensional, and each element is either +1 or -1. It is furthermore possible to find $(N!/2^R)$ permutations P, none of which are in Σ_R, such that all left cosets $P\cdot\Sigma_R$ together form exactly the total permutation group S_N; i.e., any permutation π can be written in a unique way as a product of one of the P's and a member Q of Σ_R. In other words $\pi = PQ$.

By choosing a suitable basis in the space subtended by the spin functions D_α, it is always possible to cast the irreducible representation D_S^N in that form in which all elements of the subgroup Σ_R appear in reduced form and hence are diagonal. From now on it will be assumed that D_α is that basis in which Σ_R is reduced. These spin functions θ_α will be called spin harmonics.

The Definition 2.2 of ψ_α can then be rewritten

$$\psi_\alpha = \mathcal{A}\{\theta_\alpha[2^{-R/2}\sum_Q(-1)^Q T(Q)QF_\alpha]\} \qquad (2.10)$$

where Q runs through the elements of Σ_R and $\mathcal{A}$ is the partial antisymmetrizer

$$\mathcal{A} = (2^R/N!)^{\frac{1}{2}} \sum_P(-1)^P P \qquad (2.11)$$

with P running through those elements which are needed so that all cosets $P\cdot\Sigma_R$ together yield the total permutation group S_N. Furthermore, the T(Q) are the one-dimensional representation matrices of Σ_R generated by θ_α; so that

$$2^{-R/2}\sum_Q(-1)^Q T(Q)QF_\alpha = 2^{-R/2}[e+\mathcal{E}_1(1,2)][e+\mathcal{E}_2(3,4)]$$

$$[e+\mathcal{E}_3(5,6)]\ldots[e+\mathcal{E}_R(2R-1,2R)]F_\alpha \qquad (2.12)$$

if $(-\mathcal{E}_1,-\mathcal{E}_2,\ldots-\mathcal{E}_R)$ is the representation of Σ_R in the basis θ_α. This expression is in fact the projection of F_α with respect to the irreducible representation $(\mathcal{E}_1,\mathcal{E}_2,\ldots\mathcal{E}_R)$. It follows that without loss of generality, it can be assumed that F_α belongs to the irreducible representation $(\mathcal{E}_1,\mathcal{E}_2,\ldots\mathcal{E}_R)$, i.e., to that representation of Σ_R which is conjugate to that generated by θ_α.

Expansion of space functions

In order to apply the variation principle, it is convenient to choose a set of expansion functions which are adapted to the problem, such as

$$F_\alpha = \sum_k A_{\alpha k}F_{\alpha k} \qquad (2.13)$$

where the $F_{\alpha k}$ (k = 1,2,...) are judiciously selected functions with the appropriate symmetry $(\mathcal{E}_1,\mathcal{E}_2,\ldots\mathcal{E}_R)$. Combining Equations 2.1 and 2.2, one has

$$\Psi = \sum_\alpha \sum_k A_{\alpha k}\psi_{\alpha k}, \qquad (2.14)$$

$$\psi_{\alpha k} = \mathcal{A}(\theta_\alpha F_{\alpha k}). \qquad (2.15)$$

In order to solve the variational problem, it is necessary to find one or several eigenvalues and eigenfunctions of the energy matrix between the basis functions $\mathcal{Y}_{\alpha k}$. From the definition of the partial antisymmetrizer and the representation properties of the spin factors, it can be seen that the matrix elements between the space-spin functions $\mathcal{Y}_{\alpha k}$ can be expressed in terms of those between the space functions $F_{\alpha k}$ by the formula

$$(\alpha j|H|\beta k) = (\mathcal{Y}_{\alpha j}|H|\mathcal{Y}_{\beta k}) = \sum_P (-1)^P T_{\alpha\beta}(P)(F_{\alpha j}|HP|F_{\beta k}) \qquad (2.16)$$

where the summation extends only over those permutations which are contained in the partial antisymmetrizer and $T_{\alpha\beta}(P)$ are the elements defined by Equation 2.5. Similarly the overlap integral between $\mathcal{Y}_{\alpha j}$ and $\mathcal{Y}_{\beta k}$ will be

$$(\alpha j|\beta k) = \sum_P (-1)^P T_{\alpha\beta}(P)(F_{\alpha j}|P|F_{\beta k}). \qquad (2.17)$$

The optimal wavefunction and energy are given by the solutions of

$$\sum_{\beta,k} \{(\alpha j|H|\beta k) - E(\alpha j|\beta k)\} A_{\beta k} = 0. \qquad (2.18)$$

<u>Expansion in terms of geminal products</u>

Consider now a system with an even number N of electrons and let the subgroup Σ_R be chosen as large as possible; i.e., $R = \frac{1}{2}N$.

Let $\Omega_\nu^{\mathcal{E}}(1,2)$, $\nu = 1,2,3,\ldots$ be a complete set of geminals belonging to the representation $\mathcal{E}$, i.e., symmetric if $\mathcal{E} = (+)$ and antisymmetric if $\mathcal{E} = (-)$. Then all possible geminal products (GP's)

$$\Omega_{\nu_1,\nu_2,\ldots\nu_R}^{\mathcal{E}_1,\mathcal{E}_2,\ldots\mathcal{E}_R} = \Omega_{\nu_1}^{\mathcal{E}_1}(1,2)\Omega_{\nu_2}^{\mathcal{E}_2}(3,4)\ldots\Omega_{\nu_R}^{\mathcal{E}_R}(2R-1,2R) \qquad (2.19)$$

where $(\mathcal{E}_1,\mathcal{E}_2,\ldots\mathcal{E}_R)$ is fixed and $\nu_k = 1,2,3,\ldots$ for all k's form a complete basis for any function belonging to the representation $(\mathcal{E}_1,\mathcal{E}_2,\ldots\mathcal{E}_R)$. Consequently the space-spin functions

$$\Psi_{\alpha,\nu_1,\nu_2,\ldots\nu_R} = \mathcal{A}\{\theta_\alpha\,\Omega_{\nu_1,\nu_2,\ldots\nu_R}^{\mathcal{E}_1,\mathcal{E}_2,\ldots\mathcal{E}_R}\} \qquad (2.20)$$

with

$$\nu_k = 1,2,3,\ldots \text{ for all k's}$$

form a complete basis for the expansion of Ψ_α. Each Ψ_α might be called an antisymmetric product of a spin harmonic and geminals, AP-SH-G.

A basis of particular convenience is obtained by choosing the geminals in the following simple way. Let $\omega_n(x)$ be a complete set of orthonormal orbitals. Then one can generate the following symmetric and antisymmetric geminals

$$\omega_{nn}^{+}(1,2) = \omega_n(1)\omega_n^{*}(2), \qquad (2.21)$$

$$\omega_{nm}^{+}(1,2) = [\omega_n(1)\omega_m^{*}(2) + \omega_m^{*}(1)\omega_n(2)]/\sqrt{2},\ n \neq m, \qquad (2.22)$$

$$\omega_{nm}^{-}(1,2) = [\omega_n(1)\omega_m^{*}(2) - \omega_m^{*}(1)\omega_n(2)]/\sqrt{2},\ n \neq m. \qquad (2.23)$$

The AP-SH-G's constructed from these geminals in the manner indicated by Equation 2.19 have the following simple property: *It is always possible to choose the basis of geminal products in such a way that, in any given product of geminals, any one orbital occurs only within one geminal.* In order to understand this, one observes first that an AP-SH-G made from the geminals of Equations 2.21, 2.22 and 2.23 will vanish if one particular orbital occurs more than twice. Second, _if_ a particular orbital occurs twice, then it is always permissible to arrange the geminal product so that this orbital occurs in the same geminal, and one has a geminal of the form ω_{nn}^{+} given by Equation 2.21. This is so because the linear spaces spanned by the set $\mathcal{A}(\theta_\alpha F)$, $\alpha = 0,1,2,3,\ldots$, and by the set $\mathcal{A}(\theta_\alpha \tilde{F})$, $\alpha = 0,1,2,3,\ldots$, respectively, are identical if F and $\tilde{F}$ differ merely by a permutation.

A first consequence of this admissible convention is that _any two geminals_ Ω_ν^{ε} and Ω_μ^{δ} occurring in _one_ AP-SH-G of this type are _strongly_ orthogonal to each other; i.e.,

$$\int dV_1 [\Omega_\nu^{\varepsilon}(1,2)]^* \Omega_\mu^{\delta}(1,3) = 0, \qquad (2.24)$$

and consequently, one has an antisymmetric product of a spin harmonic and _separated_ geminals, AP-SH-SG.

A second consequence is that the _AP-SH-G's constructed from the geminals of Equations 2.21, 2.22 and 2.23 form an orthonormal set._ In order to see this, consider the overlap integral of $\Psi_{\alpha;\nu_1,\nu_2\ldots}$ and $\Psi_{\alpha;\mu_1,\mu_2,\ldots}$. From Equations 2.17, 2.19 and 2.20 one finds

$$(\alpha,\mu_1,\mu_2,\ldots|\beta,\nu_1,\nu_2,\ldots) = \sum_P (-1)^P T_{\alpha\beta}(P)(\Omega_{\mu_1}^{\varepsilon_1}\Omega_{\mu_2}^{\varepsilon_2}\ldots|P|\Omega_{\nu_1}^{\delta_1}\Omega_{\nu_2}^{\delta_2}\ldots). \qquad (2.25)$$

Since P merely permutes electron coordinates, all space integrals vanish unless the two geminal products contain exactly the same orbitals. According to the adopted convention, this implies that $\Omega_{\mu_i}^{\varepsilon_i}$ and $\Omega_{\nu_j}^{\delta_j}$ contain the same orbitals, i.e., $\mu_i = \nu_j$ for all i's, and that only the identity permutation gives a non-zero contribution. Because of the latter circumstance, together with $\mathcal{E}_i = \delta_i$, the overlap integral vanishes unless the two AP-SH-G's are identical. If they are identical, one obtains unity.

Augmented Separated Pair Expansion

Augmented separated pair configurations

The separated pair approximation which has been examined in Part I can be characterized by limiting the summation in Equation 2.14 to the single term

$$\Phi_{SP} = \mathcal{A}\{\theta_0 F_{SP}\} \tag{2.26}$$

where

$$\theta_0 = 2^{-R/2}[\alpha(1)\beta(2)-\beta(1)\alpha(2)][\alpha(3)\beta(4)-\beta(3)\alpha(4)]\ldots[\alpha(N-1)\beta(N)-\beta(N-1)\alpha(N)] \tag{2.27}$$

belongs to the representation $(-,-,-,\ldots-)$ of Σ_R and F_{SP} is the optimal product of separated geminals

$$F_{SP} = \Omega_1^+(1,2)\Omega_2^+(3,4)\ldots\Omega_R^+(N-1,N) = \Lambda_1(1,2)\Lambda_2(3,4)\ldots\Lambda_R(N-1,N) \tag{2.28}$$

belonging to the representation $(+,+,+,\ldots+)$ of Σ_R with all geminals being strongly orthogonal

$$\int dV_1 \Lambda_\mu^*(1,2)\Lambda_\nu(1,3) \equiv 0 \text{ for } \mu \neq \nu. \tag{2.29}$$

If such an antisymmetric product of separated geminals (APSG) is an effective approximation, then an obvious refinement is to choose it as the leading term in the expansion of Equation 2.14, i.e., to put

$$\Psi_{00} = \Phi_{SP},\ F_{00} = F_{SP}. \tag{2.30}$$

The other terms $\Psi_{\alpha k}$ can then be expected to occur with small coefficients and, under favorable conditions, may be treated by perturbation methods.

In order to find appropriate expressions for these higher terms, it would appear natural to use once again the information furnished by the separated pair approximation. Suppose the separated geminals $\Omega_\mu^+ = \Lambda_\mu$ occurring in F_{SP} of Equation 2.30 have been expressed in terms of their natural orbitals $\phi_{\mu i} = (\mu i)$ as has been elaborated in Part I, i.e.,

$$\Lambda_\mu(1,2) = \sum_i C_{\mu i}\phi_{\mu i}(1)\phi_{\mu i}^*(2) \tag{2.31}$$

$$= \sum_i C_{\mu i}|\mu i \rangle\langle \mu i|. \tag{2.32}$$

It is then proposed that an effective basis for expansion of the higher terms $F_{\alpha k}$ is obtained by forming the AP-SH-SG's of the type defined in Equation 2.19 with the help of those orthonormal geminals which are generated from the natural orbitals $\phi_{\mu i}$ according to the definitions of Equations 2.21, 2.22 and 2.23 and the conventions discussed thereafter. These basis functions are then <u>antisymmetrized products of spin harmonics and separated geminals generated from the natural orbitals of the separated pair approximation</u>. As shown before, they form an orthogonal set.

Now the separated pair approximation Ψ_{00} itself is a linear combination of such functions; i.e.,

$$F_{00} = F_{SP} = \sum_{\nu=0}^{B-1} b_\nu G_\nu, \tag{2.33}$$

$$\Psi_{00} = \mathcal{A}(\Theta_0 F_{00}) = \sum_{\nu=0}^{B-1} b_\nu \mathcal{A}(\Theta_0 G_\nu) \tag{2.34}$$

where $G_0, G_1, \ldots G_{B-1}$ and $b_0, b_1, \ldots b_{B-1}$ denote those products of geminals constructed from natural orbitals and associated products of occupation coefficients, respectively, which appear in the expansion of F_{00}. The AP-SH-SG's formed with *all other* geminal products are therefore orthogonal to ψ_{00}; but those formed from $G_0, G_1, \ldots G_{B-1}$, although orthonormal to each other, are not orthogonal to ψ_{00}. It is therefore advisable to define a set of B orthonormal linear combinations G_ν' of the geminal products G_ν,

$$G_\nu' = \sum_{\mu=0}^{B-1} G_\mu R_{\mu\nu}, \quad \nu=0,1,2,\ldots B-1, \tag{2.35}$$

such that

$$G_0 = F_{00}. \tag{2.36}$$

Then the B functions

$$\psi_{0\nu} = \mathcal{A}(\theta_0 G_\nu') = \sum_{\mu=0}^{B-1} \mathcal{A}(\theta_0 G_\mu) R_{\mu\nu} \tag{2.37}$$

form an orthonormal set, and ψ_{00} is the separated pair approximation.

It appears that these functions $\psi_{0\nu}$ together with the AP-SH-SG's formed from the *other* geminal products (i.e., those which are not identical to one of the G_ν's) form suitable orthonormal and complete basis sets $F_{\alpha k}$ and $\psi_{\alpha k} = \mathcal{A}(\theta_\alpha F_{\alpha k})$, respectively, for the expansion of Ψ indicated by Equation 2.14. *The basis functions $\psi_{\alpha k}$ constructed in this manner will be called the augmented separated pair configurations (ASPC's). The leading term ψ_{00} will be called the separated pair configuration (SPC).*

It remains to define the orthogonal matrix R of Equation 2.35. The following two simple transformations are readily verified to accomplish the purpose.

Either

$$\left.\begin{aligned} G_\nu' &= G_\nu - [b_\nu/(1+b_0)](F_{00}+G_0) && (2.38)\\ &\text{or} \\ G_\nu' &= G_\nu - [b_\nu/(1-b_0)](F_{00}-G_0) && (2.39)\end{aligned}\right\}\text{ for } \nu \geq 1$$

corresponding to the two matrices, respectively,

$$R_{\mu\nu} = \begin{cases} b_\mu & \text{if } \nu = 0, \quad (2.40)\\ -b_\nu & \text{if } \mu = 0,\ \nu \geq 1, \quad (2.41)\\ \delta_{\mu\nu} - b_\mu b_\nu/(1+b_0) & \text{if } \mu \geq 1,\ \nu \geq 1, \quad (2.42)\end{cases}$$

and

$$R_{\mu\nu} = \begin{cases} b_\mu & \text{if } \nu = 0, \quad (2.43)\\ b_\nu & \text{if } \mu = 0,\ \nu \geq 1, \quad (2.44)\\ \delta_{\mu\nu} - b_\mu b_\nu/(1-b_0) & \text{if } \nu \geq 1,\ \mu \geq 1. \quad (2.45)\end{cases}$$

Of course other orthogonal transformations which would achieve the same purpose exist. The two transformations given seem particularly appropriate if within the separated pair approximation the term (b_0G_0) is dominant, as is in fact the case if the antisymmetrized product of the principal natural orbitals is a good approximation to the separated pair configuration. Furthermore, in order to minimize the difference between G_ν and G_ν', one will choose the set of Equations 2.38 if b_0 is positive and the set of Equations 2.39 if b_0 is negative. Normally b_0 is chosen to be positive.

Essential augmented separated pair configurations

The formal construction of an elaborate set of complex N-electron basis functions, such as the one just proposed, is justified if and only if it leads to a drastic reduction of the number of basis functions needed for an effective representation of the exact wavefunction. The crucial question is therefore how rapidly the expansion in terms of ASPC's converges. While physical intuition suggests the formulation of these basis functions and also supplies conjectures about which configurations are important, only experience in actual applications can reliably tell how many and which of the ASPC's are essential under various conditions. The selection criteria suggested in the following are extrapolations from the experiences gained with the beryllium-like systems, to be discussed in the subsequent sections. The conclusions appear reasonable enough to promise success in other systems.

Let the geminal products generated from the natural orbitals $\phi_{\mu j}$ and $\phi_{\nu k}$ be

$$(\mu j,\nu k)^{\varepsilon} = [\phi_{\mu j}(1)\,\phi_{\nu k}^{*}(2) + \phi_{\nu k}^{*}(1)\phi_{\mu j}(2)]/\sqrt{2},\quad (\mu j \neq \nu k), \tag{2.46}$$

$$(\mu j,\mu j)^{+} = \phi_{\mu j}(1)\phi_{\mu j}^{*}(2). \tag{2.47}$$

Note that $\phi_{\mu j}$ is the j-th natural orbital of the separated pair geminal Λ_{μ}. The corresponding antisymmetrized products of spin harmonics and separated geminals (AP-SH-SG's) are denoted by

$$(\mu i,\mu' i';\nu j,\nu' j';\ldots;Rr,R'r';\alpha)$$

$$=\mathcal{A}\{\Theta_{\alpha}(\mu i,\mu' i';\nu j,\nu' j';\ldots;Rr,R'r')^{\varepsilon_1,\varepsilon_2,\ldots\varepsilon_R}\} \tag{2.48}$$

where

$$(\mu i,\mu' i';\nu j,\nu' j';\ldots;Rr,R'r')^{\mathcal{E}_1,\mathcal{E}_2,\ldots\mathcal{E}_R}$$

$$= (\mu i,\mu' i')^{\mathcal{E}_1}(\nu j,\nu' j')^{\mathcal{E}_2}\ldots(Rr,R'r')^{\mathcal{E}_R} \qquad (2.49)$$

is the geminal product belonging to that representation of Σ_R which is conjugate to that of θ_α.

We shall now group all possible augmented separated pair configurations into classes:

<u>Class 0</u> consists only of the separated pair approximation (or separated pair configuration) $\Phi_{SP} = \Psi_{00}$. This function is a linear combination of all possible AP-SH-SG's of the type

$$(1i,1i;2j,2j;\ldots;Rr,Rr;0),\ (i,j,\ldots R = 0,1,\ldots) \qquad (2.50)$$

denoted by G_ν in Equations 2.33 and 2.34.

<u>Class 1</u> consists of B-1 ASPC's which are those linear combinations of the AP-SH-SG's 2.50 just quoted and are orthogonal to the separated pair function Φ_{SP} (i.e., G_ν' for $\nu \neq 0$). They are given by Equations 2.37 and 2.38 or 2.39. All members of this class have $\alpha = 0$.

<u>Class 2</u> contains all other ASPC's which have the same distribution of electrons over the <u>different</u> geminals, i.e., all other AP-SH-SG's of the type

$$(1i,1i';2j,2j';\ldots;\nu k,\nu k';\ldots;Rr,Rr';\alpha) \qquad (2.51)$$

where $\nu k \neq \nu k'$ for at least one ν. In this class various values of α are permitted. The class may be subdivided as follows:

Class 2a contains the AP-SH-SG's ($\alpha = 0$) which in the original calculations of the separated pair approximation were eliminated by expressing each geminal in terms of its natural orbitals (transformation from "single excitations" to "double excitations").

Class 2b contains such AP-SH-SG's which must be excluded from Φ_{SP} because the symmetry condition does not permit them to be included in one antisymmetrized product of geminals, such as the AP-SH-SG (K1s,K2p;L2s,L2p;α) in beryllium.

Class 3 contains all AP-SH-SG's of the type

$$(1i,1i';\ldots;(\nu-1)j,(\nu-1)j';\nu m,\mu n;(\nu+1)k,(\nu+1)k';\ldots;Rr,Rr';\alpha); \qquad (2.52)$$

i.e., in the νth geminal *one* orbital has been replaced by a natural orbital from *another* separated pair geminal Λ_μ ($\mu \neq \nu$).

Class 4 contains all other AP-SH-SG's formed from the natural orbitals of the separated pair approximation.

Based on the results of the beryllium-like systems the conjecture that *substantial energy lowerings beyond the separated pair approximation result only from ASPC's in Classes 2b and 3* is very reasonable.

Thus in beryllium from a total of about 300 possible ASPC's, only 13 ASPC's from these two classes contributed 91 per cent of the total energy lowering beyond the separated pair approximation for beryllium, and 26 from these two classes contributed 98 per cent.

Energy analysis of augmented separated pair expansion

Let us return to a general notation and write

$$\Psi = \sum_n c_n \psi_n \tag{2.53}$$

where ψ_0 shall represent the separated pair approximation, and ψ_ν for $\nu > 0$ shall represent higher ASPC's. If these latter are small enough corrections, first-order perturbation theory may be justified, and one obtains the coefficients

$$c_n = H_{0n}/(H_{00} - H_{nn}) \tag{2.54}$$

and the energy lowering

$$\Delta E = \sum_n \Delta E_{0n}, \tag{2.55}$$

$$\Delta E_{0n} = H_{0n}^{\;2}/(H_{00} - H_{nn}) \tag{2.56}$$

which yields a decomposition according to ASPC's.

A similar decomposition of the energy lowering can also be obtained if the coefficients are determined more accurately. Let

$$E = \sum_{i,j} c_i H_{ij} c_j \tag{2.57}$$

be the energy for the coefficients determined from the secular equation

$$\sum_j H_{ij} c_j = E c_i. \tag{2.58}$$

Then it is readily seen that the energy lowering $(E - H_{00})$ can be written

$$\Delta E = E - H_{00} = \sum_i \Delta E_i \tag{2.59}$$

where

$$\Delta E_i = (H_{ii} - H_{00})c_i^2 + c_i \sum_{k(\neq i)} H_{ik}c_k \tag{2.60}$$

$$= (E - H_{00})c_i^2 \tag{2.61}$$

is obtained by using Equation 2.58. If now $c_i \ll c_0$ for all $i \neq 0$, then the ΔE_i for $i \neq 0$ are third-order terms whereas ΔE_0 is a first-order term; in beryllium, e.g., one finds $(c_i/c_0)^2 < 10^{-5}$. Since $(E - H_{00})$ is already small, one has

$$\Delta E \approx \Delta E_0 = \sum_k \Delta E_{0k}', \tag{2.62}$$

$$\Delta E_{0k}' = c_0 H_{0k} c_k, \tag{2.63}$$

which provides a useful decomposition of ΔE for analyzing the contributions of the various augmented separated pair configurations.

If one desires to determine the coefficients more accurately than by first-order perturbation theory, then an iterative procedure for obtaining a specific eigenvalue is employed because very large matrices are usually encountered. The first-order perturbation results are excellent starting values for such a refinement.

From the preceding analysis it follows that the energy lowering resulting from the ASPC's are due to intershell correlations in all cases <u>except</u> for those ASPC's which are already in an APSG, i.e., G_1', G_2',... G_ν', because the energy lowering results from energy integrals between natural orbitals characteristic of two different separated geminals. This can be seen from the following arguments.

To qualify as an augmented separated pair configuration, the configuration must differ from all separated pair configurations G_ν of

Equation 2.33 by at least one orbital. Consider first the case where only one orbital is different. Suppose that the geminal Ω_1 is constructed from the two natural orbitals (1i) and (νj) for $\nu \neq 1$, whereas all other geminals Ω_δ for $\delta \neq 1$ are products of natural orbitals Ω_δ^{SP} such as occur in the construction of the separated pair approximation. Then the matrix element H_{0n} is a linear combination of terms of the form $(\Omega_1^{SP}\Omega_2^{SP}\Omega_3^{SP}\ldots|H\;|\Omega_1\Omega_2^{SP}\Omega_3^{SP}\ldots)$ and is resolved as follows: First, if $P = e$ then $H_{0n} \propto (\Omega_1^{SP}|H|\Omega_1)$, and only one space orbital is common to both geminals. The one-electron operator obviously connects orbitals characteristic of different geminals as do the two-electron operators. Second, if P is any other permutation obtained by permuting electrons between the geminals, then at least two orbitals in $\Omega_1^{SP}\Omega_2^{SP}\ldots$ will not match two orbitals in $\Omega_1\Omega_2^{SP}\ldots$; and therefore, the two-electron operator will again connect orbitals characteristic of different geminals. This argument is easily generalized to the case in which more than two orbitals are different. Hence H_{0n} gives rise to intershell interactions only.

AUGMENTED SEPARATED PAIR EXPANSION FOR BERYLLIUM-LIKE SYSTEMS

Construction of Wavefunction

Space-spin functions

For a four-electron system in a singlet state, there are two spin harmonics

$$\theta_0(1,2,3,4) = \frac{1}{2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)][\alpha(3)\beta(4) - \beta(3)\alpha(4)] \quad (2.64)$$

and

$$\begin{aligned}\theta_1(1,2,3,4) = \{&\alpha(1)\alpha(2)\beta(3)\beta(4) + \beta(1)\beta(2)\alpha(3)\alpha(4) \\ &- \frac{1}{2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)][\alpha(3)\beta(4) + \beta(3)\alpha(4)]\}/\sqrt{3}.\end{aligned} \quad (2.65)$$

The subgroup Σ_R consists of the elements e, (12), (34) and (12)(34) and appears already in reduced form: θ_0 belongs to the representation $(\mathcal{E}_1,\mathcal{E}_2) = (+,+)$; θ_1 belongs to the representation $(\mathcal{E}_1,\mathcal{E}_2) = (-,-)$. The two representations are each other's conjugate. From an arbitrary space function F, it is possible to construct F_0 and F_1 by the projections

$$F_0 = \frac{1}{2}[e + (12)][e + (34)]F \text{ belonging to } (+,+), \quad (2.66)$$

$$F_1 = \frac{1}{2}[e - (12)][e - (34)]F \text{ belonging to } (-,-). \quad (2.67)$$

The $(4!/2^2) = 6$ permutations occurring in the partial antisymmetrizer $\mathcal{A}$, as well as their representation matrices, are:

P		(13) and (24)		(14) and (23)		e and (13)(24)	
$T_{00}(P)$	$T_{01}(P)$	$\frac{1}{2}$	$-\frac{1}{2}\sqrt{3}$	$\frac{1}{2}$	$\frac{1}{2}\sqrt{3}$	1	0
$T_{10}(P)$	$T_{11}(P)$	$-\frac{1}{2}\sqrt{3}$	$\frac{1}{2}$	$\frac{1}{2}\sqrt{3}$	$-\frac{1}{2}$	0	1

. (2.68)

Using these matrix elements in the General Equation 2.16 and using further the symmetry properties of the functions F_{0k} and F_{1k} with respect to the subgroup Σ_R, one obtains for the energy matrix elements the simplified expressions

$$(\Psi_{0j}|H|\Psi_{0k}) = (F_{0j}|H\{e - 2(13) + (13)(24)\}|F_{0k}), \tag{2.69}$$

$$(\Psi_{1j}|H|\Psi_{1k}) = (F_{1j}|H\{e + 2(13) + (13)(24)\}|F_{1k}), \tag{2.70}$$

$$(\Psi_{1j}|H|\Psi_{0k}) = 2\sqrt{3}(F_{1j}|H|(13)F_{0k}). \tag{2.71}$$

The ^1S state

The basic one-electron functions for atomic systems are natural atomic orbitals of the separated pair approximation

$$(v\ell m) = f_v(r)Y_{\ell m}(\theta,\phi) \tag{2.72}$$

where the radial functions are those of the natural orbitals. The label v is, therefore, a quite general characterization of f(r). The connection with the notation in Part I is established if one replaces v with (Kn) or (Ln), respectively.

In the present context it is convenient to define, from these natural atomic orbitals, normalized "angular momentum geminals", i.e., two-electron functions which are eigenfunctions of the total spin of two electrons. They are

$$(v_1\ell_1, v_2\ell_2; LM)^{\mathcal{E}} = \sum_{m_1,m_2} (-1)^{\ell_1+\ell_2+M}(2L + 1)^{-\frac{1}{2}}\begin{pmatrix}\ell_1 & \ell_2 & L\\ m_1 & m_2 & -M\end{pmatrix}\mathcal{S}_{\mathcal{E}}(v_1\ell_1m_1)(v_2\ell_2m_2) \tag{2.73}$$

where $\begin{pmatrix}\ell_1 & \ell_2 & L\\ m_1 & m_2 & M\end{pmatrix}$ are the Wigner 3j symbols and $\mathcal{S}_{\mathcal{E}}$ is one of the two symmetrization operators

$$\mathcal{S}_+ = \{1 + (12)\}/\sqrt{2} \text{ if } v_1 \neq v_2 \text{ or } \ell_1 \neq \ell_2, \qquad (2.74)$$

$$\mathcal{S}_+ = 1 \qquad \text{if } v_1 = v_2 \text{ and } \ell_1 = \ell_2, \qquad (2.75)$$

$$\mathcal{S}_- = \{1 - (12)\}/\sqrt{2}. \qquad (2.76)$$

It is understood that in the product $(v_1\ell_1m_1)(v_2\ell_2m_2)$ the first factor depends on electron one and the second, on electron two. From these angular momentum geminals, a four-electron eigenfunction with zero eigenvalue can be formed as follows:

$$(v_1\ell_1,v_2\ell_2;v_3\ell_3,v_4\ell_4;L)^{\mathcal{E}_1,\mathcal{E}_2}$$

$$= (2L + 1)^{-\frac{1}{2}} \sum_{M=-L}^{+L} (-1)^{L+M}(v_1\ell_1,v_2\ell_2;LM)^{\mathcal{E}_1}(v_3\ell_3,v_4\ell_4;LM)^{\mathcal{E}_2} \qquad (2.77)$$

where the first factor on the right depends on electrons one and two, and the second factor depends on electrons three and four. These functions form a basis for S-type space functions which moreover belong to the representations $(\mathcal{E}_1,\mathcal{E}_2) = (+,+)$ or $(-,-)$ of Σ_2 respectively.

In slight generalization of the method outlined in the general description of the augmented separated pair expansion given above, choose as basic expansion functions these linear combinations of angular momentum geminals, defined in Equation 2.77, and the corresponding space-spin wavefunctions

$$(v_1\ell_1,v_2\ell_2;v_3\ell_3,v_4\ell_4;L;\alpha) = \mathcal{A}\{\theta_\alpha(v_1\ell_1,v_2\ell_2;v_3\ell_3,v_4\ell_4;L)^{\mathcal{E}_1,\mathcal{E}_2}\}$$

(2.78)

where $(\mathcal{E}_1,\mathcal{E}_2)$ is the representation conjugate to that of θ_α. This is possible because those properties of the natural orbitals which were important in the general discussions are shared here by the orbital sets $(v\ell m)$, $m = -\ell,-\ell+1,\ldots +\ell$. In particular, at most two of the four index pairs $(v_i\ell_i)$ in Equation 2.78 can be identical, otherwise that expression vanishes. Furthermore, if two index pairs are identical, it is assumed that they are put in the same geminal, e.g., $(v\ell,v\ell;v_3\ell_3,v_4\ell_4;L;\alpha)$. As a consequence all angular momentum geminals occurring in the expression of Equation 2.77 are strongly orthogonal to each other; thus, all previous arguments based on this premise remain valid. Furthermore, the separated pair approximation itself is a linear combination of terms of this type.

In fact, the separated pair approximation consists of the specific terms $(Kn\ell,Kn\ell;Ln'\ell',Ln'\ell';0;0)$. The augmented separated pair configurations ASPC's $\Psi_{\alpha k}$ are obtained by applying to these specific terms the orthogonal transformation defined in Equations 2.37 and by further adding all other S-type wavefunctions defined by Equations 2.20-2.23.

Determination of important configurations

Since there are well over a thousand configurations which can be constructed from the natural orbitals of the separated pair approximation Φ_4, a systematic procedure for finding the substantial contributors to the energy lowering has to be followed. In this endeavor, two kinds of considerations are helpful. First, the results obtained for the wavefunction Ψ_i can be used with advantage when proceeding to the more complicated wavefunction Ψ_{i+1}. Second, a good indication of the importance of a configuration is usually given by the second-order perturbation energy as well as by the energy lowering $c_0c_nH_{0n}$ of Equation 2.63.

In the case of the augmented separated pair expansion Ψ_2 all possible augmented separated pair configurations, 24 (in addition to the SPA and five configurations of Class 1) in all, including all possible intermediate angular momentum couplings were investigated; i.e., the ASPC's (K2p,K2p;L2p,L2p;L;α) were constructed for the geminal angular momentum $L = 0$, 1, 2 and $\alpha = 0$ and 1. However, this ASPC was found to yield energy contributions of less than 10^{-7} a.u.

In view of this result, only those 86 (in addition to the SPA and 11 configurations of Class 1) additional ASPC's were considered for Ψ_3 which had geminal angular momentum $L = 0$. Henceforth the argument L will be omitted and every ASPC will be denoted by $(Kn\ell,Kn'\ell';Ln\ell,Ln'\ell';\alpha)$. It was now further observed that all configurations which contribute more than 10^{-5} a.u. satisfy the following two criteria: (i) At least two of the four natural orbitals involved belong to the five most important NO's, viz., (K1s), (K2s), (K2p), (L2s) and (L2p). (ii) It is possible to form a geminal with angular momentum $L = 0$ from two of these specific orbitals.

For the augmented separated pair expansion Ψ_4, finally, only those 174 (in addition to the SPA and 49 configurations of Class 1) additional ASPC's which fulfilled the two conditions just mentioned were considered. Thus a total of 284 augmented separated pair configurations were examined. The importance of each configuration was not only deduced from the second-order perturbation energy $H_{0n}^2/(H_{00}-H_{nn})$, but it was further ascertained by examining the contribution $(c_0H_{0n}c_n)$ after determining the lowest eigenvalues of 80 by 80 energy matrices. In this way, 35 augmented separated pair configurations which lowered the energy by more than 10^{-5} a.u. were identified. (Eleven more which gave contributions of slightly less than 10^{-5} a.u. were omitted.) The 35 configurations together with the 50 configurations $\Psi_{0\nu}$ defined by Equation 2.37 were then included in a final calculation. The lowest eigenvalue of this 85 by 85 matrix was determined exactly, as well as by second-order perturbation theory; and it was found that, in this 85 dimensional function space, only 28 ASPC's gave contributions of 10^{-5} a.u. or more.

The ASPC's of Class 0 and Class 1, i.e., $G_0', G_1', \ldots G_\nu'$, generate intrageminal correlations and intergeminal interactions of the type discussed in the energy analysis given in Part I for the separated pair approximation. The energy lowerings resulting from the configurations of Class 1 defined by Equations 2.56 and 2.63 for the ASPE's Ψ_2, Ψ_3 and Ψ_4 gave negligible contributions for all but two or three configurations of the ions lithium -1, carbon +2, nitrogen +3 and oxygen +4 for which cases they were less than 0.00007 a.u. In these cases the total contributions are about the same as the error of the calculation. On the other hand, if the total energy for Ψ_2 and Ψ_3 is calculated by omitting the ASPC's of Class 1, then it is found to be only about 0.00003 a.u. for Ψ_2 and 0.0001 a.u. for Ψ_3 above the energy calculated by including them. The lack of regularity in the data indicates that a more accurate calculation must be performed in order to determine precisely the importance of these configurations. Since the energy lowering from these ASPC's is nearly the same as the total error of the calculated total energy values, it may be concluded that the ASPC's of Class 1 are unimportant and that the SPC is the only configuration necessary in the space spanned by G_0', G_1',...G_ν'. Therefore the ASPC's of Class 1 are excluded from the following discussion even though the reported total energies do include them.

Characteristics of contributing configurations

The 28 contributing ASPC's are listed and enumerated in Figure 27. They are divided into three groups whose definitions correspond to the classification of ASPC's in the general discussion of augmented separated pair configurations. Each contributing ASPC is denoted by a number between 1 and 28 to indicate its importance in lowering the energy of Ψ_4 beyond that of Φ_4 for the beryllium atom, which will become evident from the discussion below in connection with Figure 34. In examining these augmented separated pair configurations, the following observations appear to be pertinent.

1. The contributing configurations lower the energy by virtue of intershell correlations as has been discussed above. This appears to indicate that the intrashell correlations have been adequately taken into account by the separated pair approximation.

2. This inference is supported by considering the configurations in Class 2b, which are constructed from two K orbitals and two L orbitals. The contributing configurations are those which cannot be accommodated in the separated pair approximation because several APSG's of that type are required to construct a wavefunction with vanishing total angular momentum. In contrast, negligible contributions are found for all other configurations containing two K and two L orbitals, e.g., for those

(Class 2a) corresponding to "single excitations" between the natural orbitals of one geminal and also for those (Class 1) which correspond to the configurations G_ν' ($\nu \neq 0$) generated by the transformation described in Equation 2.37.

3. Everyone of the 28 contributing ASPC's contains at least two of the three orbitals (K1s), (L2s), (L2p), i.e., the principal and secondary natural orbitals. In fact, an ASPC containing more than two natural orbitals other than the principal and secondary ones is not expected to contribute substantially because it gives non-zero contributions to H_{0n} only by interacting with those configurations in the SPC which contain the weakly occupied natural orbitals and which therefore have as expansion coefficients the product of two weak occupation coefficients ($C_{Ki}C_{Lj}$). Twenty-six ASPC's contain K orbitals as well as L orbitals. Of these, 22 contain a geminal generated by the two principal natural orbitals, i.e., the geminal (K1s,L2s); of the remaining four, three contain the geminal (K2p,L2p), and one contains the geminal (K2s,L2s). Two of the 28 ASPC's, Numbers 12 and 22, contain orbitals from one shell only; not surprisingly, these orbitals are the four major orbitals (K1s), (K2s), (L2s) and (L2p).

4. By comparison with the configurations which do contribute, it is somewhat surprising that the ASPC's (K1s,K1s;K2p,K2p;0) and (K1s, K1s;K2s,L2s;0) give negligible energy lowerings. The lack of a substantial contribution from the latter ASPC is very likely due to its being a "single excitation" in the sense to be discussed in Observation 5.

5. Among all 28 contributing ASPC's there is no single excitation with respect to the antisymmetrized product of the principal natural

orbitals (K1s,K1s;L2s,L2s;0). The explanation clearly is that Brillouin's Theorem, which predicts vanishing second-order energy lowering for any single excitation from the Hartree-Fock antisymmetrized product, remains nearly true when the Hartree-Fock orbitals are replaced by the principal natural orbitals. Twenty-six ASPC's are two-electron excitations. The remaining two, Numbers 9 and 15, are three-electron excitations, but they involve the secondary natural orbital (L2p) twice.

Quantitative Results

Energy and expansion coefficients

The results of the final calculations are listed in Figure 28. Also included are the results obtained by other investigators who have carried out rigorous calculations beyond a separated pair approximation. Calculations within the separated pair approximations were discussed in Part I. The result of Kelly (1963, 1964) was obtained by the application of Brueckner-Goldstone type many-body type perturbation theory. The exact deviation of this value from the actual expectation value of the energy, calculated explicitly from the wavefunction, is not known with certainty, since the generated wavefunction is so complex that it has not yet been written down.

The Figure gives the energies calculated with Ψ_2, Ψ_3 and Ψ_4, as well as the energy E(ASPE) obtained by means of the extrapolation procedure derived in Part I in order to correct for the K-shell defect in the separated pair approximation, i.e.,

$$E(\text{ASPE}) = E(\text{ASPE } \Psi_4) + c_0^2\{E(\text{SP}) - E(\text{APSG } \Psi_4)\}.$$

The percentage of the correlation energy recovered by the augmented separated pair expansion is approximately constant, about 94 per cent for Ψ_4 and 96 per cent for ASPE. The absolute error ranges from 3 to 5 kcal which is near chemical accuracy. The ASPE's Ψ_2, Ψ_3 and Ψ_4 obey the virial theorem about as well as the corresponding APSG's Φ_2, Φ_3 and Φ_4. For beryllium one finds for the scale factors $\eta = (-\frac{1}{2}$ Potential Energy/ Kinetic Energy) the values

$$\begin{aligned} \eta(\text{ASPE } \Psi_2) &= 0.9993494 \\ \eta(\text{ASPE } \Psi_3) &= 1.0003817 \\ \eta(\text{ASPE } \Psi_4) &= 1.0005003. \end{aligned}$$

It is therefore likely that a variation of the orbital exponents in the augmented separated pair expansion would not substantially improve the energy.

The coefficients of the various ASPC's in each of the ASPE's determined are given in Figures 29, 30 and 31. With the data given for the corresponding APSG's, these coefficients permit the calculation of any expectation value.

Intergeminal correlations

The energy lowerings for the ASPE's Ψ_2, Ψ_3 and Ψ_4 can be partitioned according to the scheme discussed in connection with Equation 2.62. This analysis is exhibited in Figures 32, 33 and 34. The order of listing, as well as the corresponding numbering of the ASPC's, is based upon the relative importance of the energy lowerings obtained with the wavefunction Ψ_4 for the beryllium atom.

The contributions listed (except for the separated pair approximations Φ_i) are the quantities $c_0 c_n H_{0n}$. According to Equation 2.62 their sum ΔE(ASPC) should be nearly equal to the energy lowering [E(ASPE Ψ_4) - E(APSG Φ_4)]. The very close agreement between the two numbers, which is evident from the figure, is due to the smallness of the neglected terms ΔE_k for $k \neq 0$ of Equation 2.61. An explicit examination shows indeed that, in Equation 2.61, one has to substitute $c_k^2 < 10^{-5}$ and [H_{00} - E(ASPE Ψ_i)] $< 1.3 \times 10^{-3}$ a.u. Explicit calculations using Equation 2.60 gave slightly larger results presumably due to truncation errors.

By comparing the values in Figures 32, 33 and 34, one recognizes that the energy contribution of each ASPC is approximately the same for Ψ_2, Ψ_3 and Ψ_4. In general the contribution of a given ASPC improves by going to a better ASPE. This fact is analyzed in Figure 35, where the energy lowering of each ASPE is decomposed according to contributions characteristic of (i) those ASPC's which are in Ψ_2; (ii) those ASPC's which are in Ψ_3 but not in Ψ_2; (iii) those ASPC's which are in Ψ_4 but not in Ψ_3. It is seen that, e.g., for Ψ_4 the refinement of the ASPC's occurring already in Ψ_3 furnishes an energy lowering which is not negligible in comparison with that arising from the new configurations introduced by Ψ_4.

The lowering of the energy calculated with the ASPE Ψ_i beyond that calculated with the separated pair approximation Φ_i qualifies entirely as <u>inter</u>geminal correlations, as has been discussed above. In the case of beryllium, the best wavefunction Ψ_4 yields an intershell correlation energy of -0.00414 a.u. which is in noteworthy agreement with the value of -0.00497 a.u. obtained by Kelly (1963). A rough estimate of -0.00648 a.u. has been given by Tuan and Sinanoğlu (1964). The dependence of the intergeminal correlations upon the nuclear charges is plotted in Graph 3. Remarkable is the nearly linear dependence upon Z^{-1} for large Z. It appears to imply that, in the Schroedinger perturbation expansion of the total energy in terms of Z^{-1}, the intershell correlations do not contribute to the terms in Z and Z^2.

Rather surprising is the result that the energy contribution for Configuration 19 is positive for several systems (in the others it vanishes). There is no reason why all contributions have to be negative; only the total energy lowering must be negative. An examination of the expansion coefficients c_n and the matrix elements H_{0n} shows them to be positive or negative to various orders of magnitude, and a closer investigation reveals that the energy contribution ΔE_n for $n \neq 0$ is negligible because the promotion energy $c_n^2(H_{nn} - H_{00})$ is balanced partly by $c_0c_nH_{0n}$ and partly by several additional terms $c_ic_nH_{in}$, which are comparable in magnitude to $c_0c_nH_{0n}$. This is in contrast to the situation in the analysis of the geminal energy in the separated pair approximation (Part I) where the intrageminal energy contributions of the type $(c_0c_nH_{0n})$, involving the principal NO's and one other NO, were always negative and much more important than other terms in balancing the positive promotion energy. Here the appearance of the additional terms $c_ic_nH_{in}$ does not permit one to show that the expansion coefficients c_n are always opposite in sign to H_{0n}, and the fact that a particular configuration contributes to lowering the energy is more complicated to explain than the energy lowering which in the separated pair approximation is obtained from a particular NO. In the augmented separated pair expansion a configuration can help in the energy lowering either by contributing to the annihilation of ΔE_n or by contributing to the energy lowering $\Delta E_0 = \Delta E(\mathrm{ASPC})$; and under certain conditions, a particular configuration may participate more in the annihilation of ΔE_n than in the energy lowering ΔE_0. Thus $c_0 c_n H_{0n}$ may actually be positive and thereby permit some other ASPC to be more effective. This subtle interplay of ASPC's appears to be rather complicated.

Perturbation theory

In order to assess the validity and usefulness of perturbation theory, a detailed quantitative comparison is given in Figure 36 for the ASPE Ψ_3 for the beryllium atom. Listed are the coefficients of all ASPC's as predicted by first-order perturbation theory and the corresponding energy contributions as predicted by second-order perturbation theory. Also given in this Figure are the deviations of these approximate coefficients from the exact coefficients and the deviations of these approximate energy contributions from the "exact" contributions, which were given in Figure 33.

By and large the perturbation energy contributions are rather close approximations. But this is not the case for the Configuration 19 since it is clearly impossible to recover its positive contribution from perturbation theory. But also for the other ASPC's, the contributions to the energy lowering are generally seen to be overestimated by the perturbation results. This conclusion is confirmed by the results included in Figure 35. There the total energy lowerings predicted from the second-order perturbation energy are also given and compared with the exact results for all ASPE's of all systems. The difference is very small for Ψ_2, but it is considerable for Ψ_3 and Ψ_4. The largest overestimate is 10^{-3} a.u. and hence is significant in the present context.

It may also be noted that a higher total energy is obtained if to calculate the energy expectation value in a rigorous fashion one uses the normalized wavefunction Ψ_3^P, constructed from the coefficients obtained by first-order perturbation theory. One finds for beryllium:

$$(\Psi_3^P|H|\Psi_3^P) = E(\text{ASPG } \Phi_3) - 0.00313 \text{ a.u.}$$

$$(\Psi_3|H|\Psi_3) = E(\text{ASPG } \Phi_3) - 0.00342 \text{ a.u.}$$

$$\text{Second-order perturbation energy} = E(\text{ASPG } \Phi_3) - 0.00371 \text{ a.u.}$$

In conclusion, it appears that perturbation theory is useful for finding a starting point in an iteration procedure to determine the exact eigen solution of the matrix problem but that the decomposition given in Equation 2.63 is more accurate and hence preferable for an analysis of the actual energy.

LITERATURE CITED

Allen, T. L. and Shull, H.
1962. Electron pairs in the beryllium atom. J. Phys. Chem. 66: 2281.

Arai, T.
1960. Theorem on separability of electron pairs. J. Chem. Phys. 33: 95.

Bonham, R. A.
1965. On certain atomic integrals involving products of r_{ij}. J. Mol. Spectry. 15: 112.

Davidson, E. R. and Jones, L. L.
1962. Natural expansion of exact wavefunctions. II. The hydrogen-molecule ground state. J. Chem. Phys. 37: 2966.

Ebbing, D. D. and Henderson, R. C.
1965. Study of separated electron pairs in the LiH Molecule. J. Chem. Phys. 42: 2225.

Edmiston, C. K.
1963a. Analyses of electronic wave functions and chemical binding in small molecules. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology.

Edmiston, C. K.
1963b. Relation of Sinanoğlu's theory of "exact pairs" to the first iteration, beyond SCF, in separated-pair theory. J. Chem. Phys. 39: 2394.

Edmiston, C. K. and Ruedenberg, K.
1963. Localized atomic and molecular orbitals. Rev. Mod. Phys. 35: 457.

Fock, V. A.
1950. Application of two-electron functions to the theory of the chemical bond (translated title). Dokl. Akad. Nauk SSSR. 73: 735.

Geller, M., Taylor, H. S. and Levine, H. B.
1965. Many-electron-theory *ab initio* calculations for the Be atom. J. Chem. Phys. 43: 1727.

Hagstrom, S. and Shull, H.
1959. Single-center wave function for the hydrogen molecule. J. Chem. Phys. 30: 1314.

Hartmann, H. and Clementi, E.
1964. Relativistic correction for analytic Hartree-Fock wave functions. Phys. Rev. 133: A1295.

Hooke, R. and Jeeves, T. A.
1961. 'Direct search' solution of numerical and statistical problems. J. Assoc. Comp. Mach. 8: 212.

Hurley, A. C.
1952. On orbital theories of molecular structure. Unpublished Ph.D. thesis. Cambridge, England, Library, Trinity College.

Hurley, A. C., Lennard-Jones, Sir J., F. R. S. and Pople, J. A.
1953. The molecular orbital theory of chemical valency. XVI. A theory of paired-electrons in polyatomic molecules. Proc. Roy. Soc. (London) A220: 446.

Huzinaga, S.
1964. SCF method in the paired-electron approximation: technical report. Yorktown Heights, N. Y. Research Division, International Business Machines.

Hylleraas, E. A.
1929. Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von ortho-Helium. Z. Physik 54: 347.

Kapuy, E.
1958. Calculation of the energy expression in case of a wave function built from two-electron orbits. Acta Phys. Acad. Sci. Hung. 9: 237.

Kapuy, E.
1959. Density matrices for wave functions built up from non-orthogonal two-electron orbits. Acta Phys. Acad. Sci. Hung. 10: 125.

Kapuy, E.
1960a. Derivation of approximate two-electron orbitals. Acta Phys. Acad. Sci. Hung. 11: 409.

Kapuy, E.
1960b. An exact derivation of orthogonal two-electron orbitals. Acta Phys. Acad. Sci. Hung. 12: 185.

Kapuy, E.
1960c. Configuration interaction for wave functions built up from orthogonal two-electron orbitals. Acta Phys. Acad. Sci. Hung. 12: 351.

Kapuy, E.
1961a. Configuration interaction for wave functions constructed from orthogonal many-electron group orbitals. Acta Phys. Acad. Sci. Hung. 13: 345.

Kapuy, E.
1961b. Derivation of almost orthogonal two-electron orbitals. Acta Phys. Acad. Sci. Hung. 13: 461.

Kelly, H. P.
1963. Correlation effects in atoms. Phys. Rev. 131: 684.

Kelly, H. P.
1964. Many-body perturbation theory applied to atoms. Phys. Rev. 136: B896.

Kinoshita, T.
1957. Ground state of the helium atom. Phys. Rev. 105: 1490.

Kinoshita, T.
1959. Ground state of the helium atom. II. Phys. Rev. 115: 366.

Kolos, W. and Roothaan, C. C. J.
1960. Correlated orbitals for the ground state of the hydrogen molecule. Rev. Mod. Phys. 32: 205.

Kotani, M., Amemiya, A., Ishiguro, E. and Kimura, T.
1955. Table of molecular integrals. Tokyo, Japan, Maruzen Co., Ltd.

Kutzelnigg, W.
1963a. Die Lösung des quantenmechanischen Zwei-Elektronenproblems durch unmittelbare Bestimmung der natürlichen Einelectronenfunctionen. Theoret. Chim. Acta 1: 327.

Kutzelnigg, W.
1963b. Résolution du problème à deux électrons en mécanique quantique par détermination directe des orbitales naturelles. Theoret. Chim. Acta 1: 343.

Kutzelnigg, W.
1964. Direct determination of natural orbitals and natural expansion coefficients of many-electron wavefunctions. I. Natural orbitals in the geminal product approximation. J. Chem. Phys. 40: 3640.

Linderberg, J. and Shull, H.
1960. Electron correlation energy in 3- and 4-electron atoms. J. Mol. Spectry. 5: 1.

Löwdin, P. O.
1955. I. Physical interpretations by means of density matrices, natural spin-orbitals, and convergence problems in the method of configurational interaction. Phys. Rev. 97: 1474.

Löwdin, P. O.
1961. Note on the separability theorem for electron pairs. J. Chem. Phys. 35: 78.

McWeeny, R.
1959. The density matrix in many-electron quantum mechanics. I. Generalized product functions. Factorization and physical interpretation of the density matrices. Proc. Roy. Soc. (London) A253: 242.

McWeeny, R.
1960. Some recent advances in density matrix theory. Rev. Mod. Phys. 32: 335.

McWeeny, R. and Mizuno, Y.
1961. The density matrix in many-electron quantum mechanics. II. Separation of space and spin variables; spin coupling problems. Proc. Roy. Soc. (London) A259: 554.

McWeeny, R. and Ohno, K. A.
1960. A quantum mechanical study of the water molecule. Proc. Roy. Soc. (London) A255: 367.

McWeeny, R. and Sutcliffe, B. T.
1963. The density matrix in many-electron quantum mechanics. III. Generalized product functions for beryllium and four-electron ions. Proc. Roy. Soc. (London) A273: 103.

Moore, C. E.
1949. Atomic energy levels. National Bureau of Standards Circular 467.

Nazaroff, G. V. and Hirschfelder, J. O.
1963. Comparison of the Hartree-Fock orbital with the first natural spin orbital for two-electron systems. J. Chem. Phys. 39: 715.

Öhrn, Y. and Nordling, J.
1963. On the calculation of some atomic integrals containing functions of r_{12}, r_{13}, and r_{23}. J. Chem. Phys. 39: 1864.

Parks, J. M. and Parr, R. G.
1958. Theory of separated electron pairs. J. Chem. Phys. 28: 335.

Pauling, L.
1949. A resonating-valence-bond theory of metals and intermetallic compounds. Proc. Roy. Soc. (London) A196: 343.

Pekeris, C. L.
1958. Ground state of two-electron atoms. Phys. Rev. 112: 1649.

Pekeris, C. L.
1959. 1^1S and 2^3S states of helium. Phys. Rev. 115: 1216.

Ransil, B. J.
1960. Studies in molecular structure. I. Scope and summary of the diatomic molecule program. Rev. Mod. Phys. 32: 239.

Reid, C. E. and Öhrn, Y.
1963. On the calculations of real wave functions in natural form for two-electron systems. Rev. Mod. Phys. 35: 445.

Roothaan, C. C. J., Sachs, L. M. and Weiss, A. W.
1960. Analytical self-consistent field functions for the atomic configurations $1s^2$, $1s^2 2s$, and $1s^2 2s^2$. Rev. Mod. Phys. 32: 186.

Roothaan, C. C. J. and Weiss, A. W.
1960. Correlated orbitals for the ground state of heliumlike systems. Rev. Mod. Phys. 32: 194.

Shull, H. and Löwdin, P. O.
1959. Superposition of configurations and natural spin orbitals. Applications to the He problem. J. Chem. Phys. 30: 617.

Shull, H. and Prosser, F.
1964. Nature of the two-electron chemical bond. IV. Natural orbitals for He_2^{++}. J. Chem. Phys. 40: 233.

Sinanoğlu, O.
1962a. Many-electron theory of atoms and molecules. I. Shells, electron pairs vs many-electron correlations. J. Chem. Phys. 36: 706.

Sinanoğlu, O.
1962b. Many-electron theory of atoms and molecules. II. J. Chem. Phys. 36: 3198.

Spang, H. A., III
1962. A review of minimization techniques for nonlinear functions. SIAM [Soc. for Ind. and Appl. Math.] Review 4: 343.

Szász, L.
1959. Über die Erweiterung der Hartree-Fockschen Näherung durch Korrelationsfunction. Z. Naturforsch. 14a: 1014.

Szász, L.
1960. Über die Berechnung der Korrelationsenergie der Atomaelectronen. Z. Naturforsch. 15a: 909.

Szász, L.
1961. On the evaluation of integrals occurring in the theory of the correlated electronic wave functions. J. Chem. Phys. 35: 1072.

Szász, L.
1962a. Atomic many-body problem. I. General theory of the correlated wave functions. Phys. Rev. 126: 169.

Szász, L.
1962b. Atomic many-body problem. II. The matrix components of the Hamiltonian with respect to correlated wave functions. J. Math. Phys. 3: 1147.

Szász, L.
1963a. Pair correlations in the Be atom. Phys. Rev. Letters 3: 263.

Szász, L.
1963b. Formulation of the quantum mechanical many-body problem in terms of one- and two-particle functions. Phys. Rev. Letters 4: 267.

Tuan, D. F. and Sinanoğlu, O.
1964. Many-electron theory of atoms and molecules. IV. Be atom and its ions. J. Chem. Phys. 41: 2677.

Wasserman, A. L.
1963. The hydrogen molecule-ion as a superposition of atomic orbitals. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology.

Watson, R. E.
1960. Approximate wave functions for atomic Be. Phys. Rev. 119: 170.

Watson, R. E.
1961. The two-configuration approximation for four-electron ions. Ann. Phys. (N. Y.) 13: 250.

Weiss, A. W.
1961. Configuration interaction in simple atomic systems. Phys. Rev. 122: 1826.

ACKNOWLEDGMENTS

The author would like to express his appreciation to Professor Klaus Ruedenberg for suggesting the problem and for his advice and guidance during the course of this investigation.

Appreciation is also extended to John Jordan for his assistance in writing some of the computer programs, to John Linderblood for his conscientious execution of the programs and to Al Kukala for his valuable assistance.

The author is deeply indebted to his wife Brunhilde for her help in the preparation of this manuscript.

APPENDIX

Effect on energy of using maximum number of natural orbitals in separated pair approximations to the beryllium atom wavefunction

APSG[a]	Basis set[b]	Energy
Φ_2	b_2	-14.64809
Φ_2	b_3	-14.65292
Φ_3	b_3	-14.65515

[a] In Φ_2, Λ_K contains three natural orbitals and Λ_L contains two natural orbitals. In Φ_3, Λ_K contains six natural orbitals and Λ_L contains two natural orbitals. Φ_2 and Φ_3 are defined in Figure 4.

[b] b_2 = (1sK, 2sK, 2pK, 2sL, 2pL) and $b_3 = b_2$ + (3sK, 3pK, 3dK).

Figure 1. Effect on energy of using maximum number of natural orbitals in separated pair approximations to the beryllium atom wavefunction

Effect on energy of optimizing the transformation matrix T[a] in separated pair approximations to the beryllium atom wavefunction

Natural orbitals in		Energy calculated with		
K-geminal	L-geminal	T = unit matrix	Best T	Energy improvement
K1s, K2s	L2s	-14.56832	-14.58433	-0.01601
K1s, K2s, K3s	L2s	-14.56875	-14.58703	-0.01828
K1s, K2s	L2s, L2p	-14.61144	-14.62727	-0.01583
K1s, K2s, K2p	L2s, L2p	-14.63269	-14.64809	-0.01540
K1s, K2s, K2p	L2s, L2p, L3d	-14.63306	-14.64848	-0.01542

[a] T is the orthogonal transformation which generates the natural orbitals from a basis of Schmidt orthogonalized Slater-type atomic orbitals. In all cases, orbital exponents and occupation coefficients are optimized.

Figure 2. Effect on energy of optimizing the transformation matrix T in separated pair approximations to the beryllium atom wavefunction

Energy lowering due to addition of various natural orbitals to separated pair approximations of the beryllium atom wavefunction[a]

Energy lowering	NO's in K-geminal									NO's in L-geminal			
	K2s	K3s	K4s	K2p	K3p	K4p	K3d	K4d	K4f	L3s	L2p	L3p	L3d
Maximum	0.02760	0.00270	0.00044	0.02278	0.00208		0.00260		0.00060	0.00068	0.04319	0.00008	0.00056
Minimum	0.02735	0.00254	0.00035	0.02035	0.00207		0.00257		0.00060	0.00060	0.04144	0.00007	0.00037
Weighted average	0.0274	0.0026	0.0004	0.0214	0.0021	0.0002[b]	0.0025	0.0003[b]	0.0006	0.0006	0.0423	0.0001	0.0004
Number of cases calculated	4	3	2	8	2		7		3	2	9	2	7

[a] The difference between the optimal energies calculated from separated pair approximations including and not including the indicated NO is given. For each NO there exists a corresponding orthogonalized STAO.

[b] Average was estimated from the trend of data.

Figure 3. Energy lowering due to addition of various natural orbitals to separated pair approximations of the beryllium atom wavefunction

Natural orbitals used with each geminal for various separated pair approximations in this investigation

APSG	NO's in K-geminal	NO's in L-geminal	Accuracy of energy
Φ_1	K1s	L2s	0.1
Φ_2	K1s, K2s, K2p	L2s, L2p	0.01
Φ_3	K1s, K2s, K3s, K2p, K3p, K3d	L2s, L2p	0.001
Φ_4	K1s, K2s, K3s, K4s, K2p, K3p, K4p, K3d, K4d, K4f	L2s, L3s, L2p, L3p, L3d	0.0001

Figure 4. Natural orbitals used with each geminal for various separated pair approximations in this investigation

Orbital exponents of Slater-type atomic orbitals used in various separated pair approximations to the beryllium-like atomic wavefunctions

STAO	Li^-	Be	B^+	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
Separated pair approximation Φ_1								
1sK	2.688	3.685	4.675	5.665	6.654	7.641	8.624	9.616
2sL	0.485	0.955	1.397	1.829	2.259	2.688	3.114	3.542
Separated pair approximation Φ_2								
1sK	2.473	3.405	4.317	5.229	6.141	7.045	7.941	8.865
2sK	3.196	4.292	5.292	6.256	7.228	8.132	9.096	10.026
2pK	3.965	5.485	6.965	8.509	10.001	11.693	13.180	14.790
2sL	0.509	0.993	1.457	1.923	2.383	2.851	3.315	3.777
2pL	0.492	0.978	1.454	1.932	2.414	2.894	3.400	3.880
Separated pair approximation Φ_3								
1sK	2.496	3.417	4.340	5.271	6.188	7.127	8.060	8.991
2sK	3.181	4.222	5.247	6.156	7.125	8.090	8.939	9.772
3sK	3.719	5.068	6.293	7.302	8.387	9.380	10.409	11.398
2pK	4.156	5.565	7.090	8.699	10.304	11.981	13.626	15.135
3pK	4.780	6.270	7.880	9.598	11.464	13.178	14.796	16.614
3dK	5.644	7.730	9.816	11.768	13.752	15.804	17.656	19.608
2sL	0.510	0.997	1.472	1.943	2.414	2.885	3.366	3.829
2pL	0.491	0.984	1.465	1.948	2.429	2.922	3.397	3.890
Separated pair approximation Φ_4								
1sK	2.496	3.417	4.340	5.271	6.188	7.127	8.060	8.991
2sK	3.181	4.222	5.247	6.156	7.125	8.090	8.939	9.772
3sK	3.719	5.068	6.293	7.302	8.387	9.380	10.409	11.398
4sK	4.655	5.955	7.155	8.255	9.355	10.455	11.555	12.655
2pK	4.156	5.565	7.090	8.699	10.304	11.981	13.626	15.135
3pK	4.780	6.270	7.880	9.598	11.464	13.178	14.796	16.614
4pK	5.400	7.000	8.600	10.300	12.100	13.900	15.700	17.500
3dK	5.644	7.730	9.816	11.768	13.752	15.804	17.656	19.608
4dK	6.330	8.330	10.330	12.330	14.330	16.330	18.330	20.330
4fK	8.130	10.530	12.930	15.330	17.730	20.130	22.530	24.930
2sL	0.510	0.997	1.472	1.943	2.414	2.885	3.366	3.829
3sL	0.510	1.000	1.480	1.950	2.420	2.890	3.370	3.840
2pL	0.491	0.984	1.465	1.948	2.429	2.922	3.397	3.890
3pL	0.510	1.000	1.480	1.960	2.440	2.930	3.420	3.900
3dL	0.726	1.216	1.696	2.176	2.656	3.136	3.616	4.096

Figure 5. Orbital exponents of Slater-type atomic orbitals used in various separated pair approximations to the beryllium-like atomic wavefunctions

Polynomial approximations to orbital exponents[a]

STAO	c_0	c_1	c_2	Δ
		Separated pair approximation Φ_1		
1sK	-0.29572	0.99715	-0.00063	0.001
2sL	-0.88578	0.46809	-0.00259	0.006
		Separated pair approximation Φ_2		
1sK	-0.29441	0.92854	-0.00135	0.005
2sK	0.39698	0.96812		0.04
2pK	-0.73030	1.54674		0.05
2sL	-0.90759	0.47670	-0.00084	0.003
2pL	-0.96360	0.48370		0.007
		Separated pair approximation Φ_3		
1sK	-0.25437	0.91337	0.00113	0.002
2sK	0.46138	0.94310		0.06
3sK	0.71800	1.08100		0.1
2pK	-0.75590	1.58852		0.07
3pK	-0.51062	1.70510		0.08
3dK	-0.22559	1.99198		0.06
2sL	-0.92826	0.48295	-0.00071	0.003
2pL	-0.95943	0.48464		0.003

[a] Listed are the coefficients of the approximation $c_0 + c_1 Z + c_2 Z^2$. It yields the STAO exponents reported in Figure 5 with a mean absolute deviation Δ.

Figure 6. Polynomial approximations to orbital exponents

Scale factors for various separated pair approximations to beryllium-like atomic wavefunctions[a]

APSG	Li^-	Be	B^+	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
Φ_1	1.0002789	0.9999542	1.0001841	1.0000951	0.9999204	0.9998759	1.0002927	0.9996968
Φ_2	0.9977483	0.9991997	0.9996603	0.9994723	0.9996715	0.9995272	0.9995502	0.9996604
Φ_3	0.9997857	1.0001876	1.0000937	0.9999798	1.0001115	0.9999441	0.9999396	1.0001216
Φ_4	0.9997825	1.0002778	1.0000298	0.9999759	0.9999934	0.9999065	0.9999153	1.0002060

[a] Listed are the values of $\eta = (-\frac{1}{2}$ Potential Energy$)/($Kinetic Energy$)$.

Figure 7. Scale factors for various separated pair approximations to beryllium-like atomic wavefunctions

Expansion coefficients of natural orbitals of separated pair approximation Φ_2 in terms of Schmidt orthogonalized Slater-type atomic orbitals

Lithium -1

	K1s	L2s	K2s	L2p	K2p
$(1sK_\perp)$	0.99814950	0.01848357	0.05792978	0.00000000	0.00000000
$(2sL_\perp)$	-0.01837111	0.99982812	-0.00247343	0.00000000	0.00000000
$(2sK_\perp)$	-0.05796554	0.00140462	0.99831755	0.00000000	0.00000000
$(2pL_\perp)$	0.00000000	0.00000000	0.00000000	0.99999684	-0.00250167
$(2pK_\perp)$	0.00000000	0.00000000	0.00000000	0.00250167	0.99999684

Beryllium

	K1s	L2s	K2s	L2p	K2p
$(1sK_\perp)$	0.99794835	0.03532755	0.05339424	0.00000000	0.00000000
$(2sL_\perp)$	-0.03549423	0.99936748	0.00217634	0.00000000	0.00000000
$(2sK_\perp)$	-0.05328358	-0.00406706	0.99857110	0.00000000	0.00000000
$(2pL_\perp)$	0.00000000	0.00000000	0.00000000	0.99999698	-0.00244981
$(2pK_\perp)$	0.00000000	0.00000000	0.00000000	0.00244981	0.99999698

Boron +1

	K1s	L2s	K2s	L2p	K2p
$(1sK_\perp)$	0.99754154	0.04417723	0.05439794	0.00000000	0.00000000
$(2sL_\perp)$	-0.04461200	0.99898116	0.00680355	0.00000000	0.00000000
$(2sK_\perp)$	-0.05404196	-0.00921363	0.99849610	0.00000000	0.00000000
$(2pL_\perp)$	0.00000000	0.00000000	0.00000000	0.99999644	-0.00266136
$(2pK_\perp)$	0.00000000	0.00000000	0.00000000	0.00266136	0.99999644

Carbon +2

	K1s	L2s	K2s	L2p	K2p
$(1sK_\perp)$	0.99727273	0.04881247	0.05535684	0.00000000	0.00000000
$(2sL_\perp)$	-0.04951430	0.99870854	0.01137774	0.00000000	0.00000000
$(2sK_\perp)$	-0.05472998	-0.01408766	0.99840176	0.00000000	0.00000000
$(2pL_\perp)$	0.00000000	0.00000000	0.00000000	0.99999542	-0.00302176
$(2pK_\perp)$	0.00000000	0.00000000	0.00000000	0.00302176	0.99999542

Nitrogen +3

	K1s	L2s	K2s	L2p	K2p
$(1sK_\perp)$	0.99713153	0.05106280	0.05586751	0.00000000	0.00000000
$(2sL_\perp)$	-0.05196794	0.99853797	0.01486954	0.00000000	0.00000000
$(2sK_\perp)$	-0.05502656	-0.01773021	0.99832741	0.00000000	0.00000000
$(2pL_\perp)$	0.00000000	0.00000000	0.00000000	0.99999510	-0.00312513
$(2pK_\perp)$	0.00000000	0.00000000	0.00000000	0.00312513	0.99999510

Figure 8. Expansion coefficients of natural orbitals of separated pair approximation Φ_2 in terms of Schmidt orthogonalized Slater-type atomic orbitals

Oxygen +4

	K1s	L2s	K2s	L2p	K2p
$(1sK_\perp)$	0.99693677	0.05313865	0.05738673	0.00000000	0.00000000
$(2sL_\perp)$	-0.05427259	0.99835684	0.01838427	0.00000000	0.00000000
$(2sK_\perp)$	-0.05631553	-0.02144248	0.99818269	0.00000000	0.00000000
$(2pL_\perp)$	0.00000000	0.00000000	0.00000000	0.99999377	-0.00352238
$(2pK_\perp)$	0.00000000	0.00000000	0.00000000	0.00352238	0.99999377

Fluorine +5

	K1s	L2s	K2s	L2p	K2p
$(1sK_\perp)$	0.99675133	0.05517358	0.05867332	0.00000000	0.00000000
$(2sL_\perp)$	-0.05646151	0.99819376	0.02052318	0.00000000	0.00000000
$(2sK_\perp)$	-0.05743501	-0.02376930	0.99806619	0.00000000	0.00000000
$(2pL_\perp)$	0.00000000	0.00000000	0.00000000	0.99999570	-0.00292663
$(2pK_\perp)$	0.00000000	0.00000000	0.00000000	0.00292663	0.99999570

Neon +6

	K1s	L2s	K2s	L2p	K2p
$(1sK_\perp)$	0.99680759	0.05476245	0.05809975	0.00000000	0.00000000
$(2sL_\perp)$	-0.05619253	0.99814865	0.02327163	0.00000000	0.00000000
$(2sK_\perp)$	-0.05671778	-0.02646211	0.99803946	0.00000000	0.00000000
$(2pL_\perp)$	0.00000000	0.00000000	0.00000000	0.99999462	-0.00327210
$(2pK_\perp)$	0.00000000	0.00000000	0.00000000	0.00327210	0.99999462

Figure 8. (Continued)

Expansion coefficients of natural orbitals of separated pair approximation Φ_3 in terms of Schmidt orthogonalized Slater-type atomic orbitals[a]

Lithium -1

	K1s	L2s	K2s	K3s		L2p	K2p	K3p
$(1sK_\perp)$	0.99870330	0.01745286	0.04520518	-0.01559951	$(2pL_\perp)$	0.99999761	-0.00205552	0.00060834
$(2sL_\perp)$	-0.01744660	0.99984698	-0.00017745	0.00116636	$(2pK_\perp)$	0.00210828	0.99440330	-0.10562854
$(2sK_\perp)$	-0.04740007	-0.00042255	0.97908905	-0.19783172	$(3pK_\perp)$	-0.00038781	0.10562959	0.99440535
$(3sK_\perp)$	0.00634866	-0.00099735	0.19834517	0.98011101				

Beryllium

	K1s	L2s	K2s	K3s		L2p	K2p	K3p
$(1sK_\perp)$	0.99816009	0.03508195	0.04840272	-0.01013286	$(2pL_\perp)$	0.99999626	0.00082965	0.00258285
$(2sL_\perp)$	-0.03548461	0.99933686	0.00788415	0.00207058	$(2pK_\perp)$	-0.00059842	0.99609618	-0.08827151
$(2sK_\perp)$	-0.04903651	-0.00926455	0.98940685	-0.13632082	$(3pK_\perp)$	-0.00264600	0.08826964	0.99609303
$(3sK_\perp)$	0.00353619	-0.00300489	0.13663380	0.99061062				

Boron +1

	K1s	L2s	K2s	K3s		L2p	K2p	K3p
$(1sK_\perp)$	0.99784586	0.04273654	0.04913384	-0.00792208	$(2pL_\perp)$	0.99999152	0.00224091	0.00343589
$(2sL_\perp)$	-0.04354084	0.99892276	0.01582054	0.00262332	$(2pK_\perp)$	-0.00192407	0.99597629	-0.08959520
$(2sK_\perp)$	-0.04900035	-0.01755764	0.99233398	-0.11208723	$(3pK_\perp)$	-0.00362284	0.08958783	0.99597224
$(3sK_\perp)$	0.00254304	-0.00427703	0.11228728	0.99366317				

Carbon +2

	K1s	L2s	K2s	K3s		L2p	K2p	K3p
$(1sK_\perp)$	0.99775195	0.04541664	0.04883549	-0.00656947	$(2pL_\perp)$	0.99999087	0.00237185	0.00353114
$(2sL_\perp)$	-0.04656262	0.99864341	0.02304582	0.00343141	$(2pK_\perp)$	-0.00199993	0.99479892	-0.10183746
$(2sK_\perp)$	-0.04810276	-0.02494673	0.99546609	-0.07817077	$(3pK_\perp)$	-0.00375432	0.10182947	0.99479468
$(3sK_\perp)$	0.00296339	-0.00509423	0.07829987	0.99691225				

Figure 9. Expansion coefficients of natural orbitals of separated pair approximation Φ_3 in terms of Schmidt orthogonalized Slater-type atomic orbitals

Nitrogen +3

	K1s	L2s	K2s	K3s		L2p	K2p	K3p
$(1sK_\perp)$	0.99759595	0.04771866	0.04996208	-0.00533704	$(2pL_\perp)$	0.99999334	0.00174989	0.00315105
$(2sL_\perp)$	-0.04915484	0.99837917	0.02837190	0.00415579	$(2pK_\perp)$	-0.00139778	0.99409862	-0.10846915
$(2sK_\perp)$	-0.04877487	-0.03046626	0.99648820	-0.06085592	$(3pK_\perp)$	-0.00332226	0.10846404	0.99409461
$(3sK_\perp)$	0.00256506	-0.00575924	0.06090525	0.99812338				

Oxygen +4

	K1s	L2s	K2s	K3s		L2p	K2p	K3p
$(1sK_\perp)$	0.99766687	0.04759494	0.04877385	-0.00404587	$(2pL_\perp)$	0.99999357	0.00172051	0.00311735
$(2sL_\perp)$	-0.04925040	0.99823608	0.03281280	0.00514232	$(2pK_\perp)$	-0.00134404	0.99313305	-0.11698131
$(2sK_\perp)$	-0.04725493	-0.03492667	0.99756571	-0.03754221	$(3pK_\perp)$	-0.00329721	0.11697638	0.99312913
$(3sK_\perp)$	0.00251723	-0.00625645	0.03750667	0.99927346				

Fluorine +5

	K1s	L2s	K2s	K3s		L2p	K2p	K3p
$(1sK_\perp)$	0.99768998	0.04756170	0.04835646	-0.00371188	$(2pL_\perp)$	0.99999526	0.00101818	0.00286028
$(2sL_\perp)$	-0.04941776	0.99802243	0.03841030	0.00577060	$(2pK_\perp)$	-0.00065860	0.99240493	-0.12301085
$(2sK_\perp)$	-0.04651130	-0.04058018	0.99785260	-0.02189968	$(3pK_\perp)$	-0.00296381	0.12300843	0.99240105
$(3sK_\perp)$	0.00297068	-0.00647305	0.02181625	0.99973638				

Neon +6

	K1s	L2s	K2s	K3s		L2p	K2p	K3p
$(1sK_\perp)$	0.99769781	0.04725102	0.04861207	-0.00165475	$(2pL_\perp)$	0.99999658	0.00034928	0.00253441
$(2sL_\perp)$	-0.04924973	0.99791485	0.04105998	0.00734704	$(2pK_\perp)$	-0.00007947	0.99439930	-0.10568648
$(2sK_\perp)$	-0.04650140	-0.04353935	0.99761007	0.02674877	$(3pK_\perp)$	-0.00255713	0.10568598	0.99439607
$(3sK_\perp)$	0.00325789	-0.00609126	-0.02691647	0.99961357				

---

[a] The expansion coefficient for the (K3d) NO is unity because this NO is identical to the (3dK) STAO.

Figure 9. (Continued)

Expansion coefficients of natural orbitals of separated pair approximation Φ_4 in terms of Schmidt orthogonalized Slater-type atomic orbitals ^{a}

Lithium -1

	K1s	L2s	K2s	K3s	L3s	K4s
(1s$K_\perp$)	0.99868747	0.01815963	0.04524306	-0.01508291	0.00360403	0.00240394
(2s$L_\perp$)	-0.01815460	0.99983281	-0.00020586	0.00123700	-0.00047659	0.00160871
(2s$K_\perp$)	-0.04746837	-0.00047089	0.97843745	-0.18958551	0.05105886	0.04308762
(3s$K_\perp$)	0.00632001	-0.00100033	0.19747332	0.97087347	-0.11963578	-0.06367776
(3s$L_\perp$)	-0.00043021	0.00028182	-0.02735892	0.12846355	0.99127127	0.01138056
(4s$K_\perp$)	0.00008130	-0.00170388	-0.02947024	0.06877248	-0.02117140	0.99697073

	L2p	K2p	K3p	L3p	K4p
(2p$L_\perp$)	0.99999703	-0.00197086	0.00062365	-0.00116850	0.00019955
(2p$K_\perp$)	0.00202762	0.99439820	-0.10290515	0.00702968	0.02299597
(3p$K_\perp$)	-0.00040902	0.10525131	0.98452034	-0.02563381	-0.13778313
(3p$L_\perp$)	0.00116141	-0.00373388	0.01680041	0.99750944	-0.06839075
(4p$K_\perp$)	-0.00022585	-0.00872646	0.14088003	0.06532201	0.98783074

	K3d	L3d	K4d
(3d$K_\perp$)	0.99622647	0.02235009	-0.08386458
(3d$L_\perp$)	-0.02146891	0.99970456	0.01139450
(4d$K_\perp$)	0.08409448	-0.00955102	0.99641199

Beryllium

	K1s	L2s	K2s	K3s	L3s	K4s
(1s$K_\perp$)	0.99811865	0.03632011	0.04951845	-0.00858806	0.00012720	0.00343317
(2s$L_\perp$)	-0.03673012	0.99928539	0.00803999	0.00273933	0.00265130	-0.00001229
(2s$K_\perp$)	-0.04896734	-0.00949263	0.99131275	-0.11049541	0.00770395	0.05041709
(3s$K_\perp$)	0.00337069	-0.00320605	0.11998079	0.95749478	-0.09918217	-0.24279408
(3s$L_\perp$)	0.00069050	-0.00288732	0.00524373	0.08478526	0.99398579	-0.06904416
(4s$K_\perp$)	-0.00009553	-0.00063291	-0.02137324	0.25243633	0.04569943	0.96629704

	L2p	K2p	K3p	L3p	K4p
(2p$L_\perp$)	0.99996579	0.00114323	0.00407688	0.00300590	0.00105970
(2p$K_\perp$)	-0.00088307	0.99683805	-0.07321494	0.00312590	0.03069934
(3p$K_\perp$)	-0.00378763	0.07677167	0.98606371	-0.05884377	-0.13530383
(3p$L_\perp$)	-0.00304918	0.00351373	0.04373666	0.99284996	-0.11096940
(4p$K_\perp$)	-0.00191387	-0.02014658	0.14278661	0.10376586	0.98409088

	K3d	L3d	K4d
(3d$K_\perp$)	0.99211734	0.03833239	-0.11930490
(3d$L_\perp$)	-0.03586733	0.99909769	0.02274175
(4d$K_\perp$)	0.12006902	-0.01828334	0.99259711

Figure 10. Expansion coefficients of natural orbitals of separated pair approximation Φ_4 in terms of Schmidt orthogonalized Slater-type atomic orbitals

Boron +1

	K1s	L2s	K2s	K3s	L3s	K4s
$(1sK_\perp)$	0.99780974	0.04352568	0.04907825	-0.00766143	-0.00119863	0.00346694
$(2sL_\perp)$	-0.04433668	0.99888572	0.01590199	0.00271876	-0.00077301	0.00053373
$(2sK_\perp)$	-0.04900574	-0.01770208	0.99144968	-0.10646846	-0.00525690	0.05430328
$(3sK_\perp)$	0.00254424	-0.00430881	0.11447684	0.96237775	-0.12186676	-0.21411934
$(3sL_\perp)$	0.00123369	0.00024871	0.02121719	0.10344843	0.99055351	-0.08746590
$(4sK_\perp)$	-0.00012543	-0.00064198	-0.02846537	0.22743223	0.06262931	0.97136058

	L2p	K2p	K3p	L3p	K4p
$(2pL_\perp)$	0.99998988	0.00236877	0.00357579	-0.00030436	0.00124350
$(2pK_\perp)$	-0.00209045	0.99593195	-0.08514148	0.00237205	0.02932825
$(3pK_\perp)$	-0.00366331	0.08724113	0.98905417	-0.08342256	-0.08478064
$(3pL_\perp)$	0.00022502	0.00810878	0.06920097	0.98558576	-0.15416232
$(4pK_\perp)$	-0.00148183	-0.02090064	0.09859456	0.14715828	0.98396363

	K3d	L3d	K4d
$(3dK_\perp)$	0.99239422	0.05894358	-0.10807100
$(3dL_\perp)$	-0.05638967	0.99805600	0.02654008
$(4dK_\perp)$	0.10942530	-0.02024413	0.99378883

Carbon +2

	K1s	L2s	K2s	K3s	L3s	K4s
$(1sK_\perp)$	0.99772502	0.04598949	0.04868147	-0.00646204	-0.00209613	0.00364716
$(2sL_\perp)$	-0.04714776	0.99860958	0.02323368	0.00354859	-0.00138736	0.00107613
$(2sK_\perp)$	-0.04808171	-0.02522155	0.99331670	-0.07587923	-0.03390987	0.05887167
$(3sK_\perp)$	0.00297654	-0.00516831	0.07974625	0.96920882	-0.14690148	-0.18071702
$(3sL_\perp)$	0.00085577	-0.00007779	0.04938895	0.12621652	0.98547181	-0.10234545
$(4sK_\perp)$	-0.00013517	-0.00071639	-0.04016176	0.19720835	0.07815982	0.97641505

	L2p	K2p	K3p	L3p	K4p
$(2pL_\perp)$	0.99998917	0.00243459	0.00365101	-0.00066689	0.00130616
$(2pK_\perp)$	-0.00210987	0.99489348	-0.09587046	0.00447947	0.03116018
$(3pK_\perp)$	-0.00377996	0.09839782	0.98636298	-0.09261369	-0.09388291
$(3pL_\perp)$	0.00059557	0.00833008	0.07432285	0.98112965	-0.17830001
$(4pK_\perp)$	-0.00152104	-0.02071636	0.11117268	0.16966648	0.97899047

	K3d	L3d	K4d
$(3dK_\perp)$	0.99359543	0.06807923	-0.09018477
$(3dL_\perp)$	-0.06554230	0.99737422	0.03080271
$(4dK_\perp)$	0.09204499	-0.02469452	0.99544857

Figure 10. (Continued)

Nitrogen +3

	K1s	L2s	K2s	K3s	L3s	K4s
(1s$K_\perp$)	0.99753608	0.04891778	0.04976873	-0.00538277	-0.00286564	0.00374448
(2s$L_\perp$)	-0.05035834	0.99831716	0.02832789	0.00418941	-0.00182309	0.00167451
(2s$K_\perp$)	-0.04876001	-0.03058065	0.99356264	-0.06112862	-0.04430855	0.06180462
(3s$K_\perp$)	0.00256550	-0.00577637	0.06266867	0.97933123	-0.13521149	-0.13660236
(3s$L_\perp$)	0.00098666	-0.00009556	0.05852948	0.11533729	0.98425352	-0.12048052
(4s$K_\perp$)	-0.00017121	-0.00077999	-0.04690446	0.15434950	0.10482360	0.98131926

	L2p	K2p	K3p	L3p	K4p
(2p$L_\perp$)	0.99999129	0.00196846	0.00336923	-0.00021768	0.00132138
(2p$K_\perp$)	-0.00166657	0.99463697	-0.09849474	0.00379760	0.03127834
(3p$K_\perp$)	-0.00341375	0.10101224	0.98607813	-0.09043213	-0.09620957
(3p$L_\perp$)	0.00020900	0.00919821	0.07033578	0.97923864	-0.18989424
(4p$K_\perp$)	-0.00159536	-0.02011942	0.11397237	0.18138124	0.97657755

	K3d	L3d	K4d
(3d$K_\perp$)	0.99284320	0.07588640	-0.09221488
(3d$L_\perp$)	-0.07301208	0.99674590	0.03415845
(4d$K_\perp$)	0.09450697	-0.02718119	0.99515304

Oxygen +4

	K1s	L2s	K2s	K3s	L3s	K4s
(1s$K_\perp$)	0.99764693	0.04798246	0.04854919	-0.00422273	-0.00286797	0.00384989
(2s$L_\perp$)	-0.04965867	0.99820028	0.03313889	0.00521991	-0.00210575	0.00206337
(2s$K_\perp$)	-0.04723853	-0.03537829	0.99406187	-0.04025158	-0.04879750	0.06600004
(3s$K_\perp$)	0.00252578	-0.00639735	0.03979286	0.97856119	-0.16037810	-0.12274217
(3s$L_\perp$)	0.00089896	-0.00042977	0.06285750	0.14061241	0.97850952	-0.13709515
(4s$K_\perp$)	-0.00019114	-0.00076841	-0.05339242	0.14484631	0.12001661	0.98069572

	L2p	K2p	K3p	L3p	K4p
(2p$L_\perp$)	0.99999188	0.00177861	0.00320224	-0.00096055	0.00127318
(2p$K_\perp$)	-0.00146324	0.99385579	-0.10600003	0.00518022	0.03138879
(3p$K_\perp$)	-0.00333787	0.10826344	0.98584914	-0.09757220	-0.08275694
(3p$L_\perp$)	0.00092916	0.00972531	0.07835331	0.97571567	-0.20431382
(4p$K_\perp$)	-0.00134746	-0.02077315	0.10351648	0.19603758	0.97489496

	K3d	L3d	K4d
(3d$K_\perp$)	0.99160544	0.07623860	-0.10443303
(3d$L_\perp$)	-0.07236189	0.99655880	0.04042590
(4d$K_\perp$)	0.10715569	-0.03252957	0.99370994

Figure 10. (Continued)

Fluorine +5

	K1s	L2s	K2s	K3s	L3s	K4s
(1s$K_\perp$)	0.99767742	0.04781100	0.04812855	-0.00339642	-0.00314441	0.00394040
(2s$L_\perp$)	-0.04967286	0.99800482	0.03825484	0.00603238	-0.00335575	0.00270644
(2s$K_\perp$)	-0.04650447	-0.04070604	0.99351959	-0.01539779	-0.06304121	0.06990839
(3s$K_\perp$)	0.00296695	-0.00650905	0.01204514	0.98069437	-0.16427989	-0.10513678
(3s$L_\perp$)	0.00055894	-0.00004484	0.07395153	0.14795893	0.97661104	-0.13736740
(4s$K_\perp$)	-0.00015985	-0.00074737	-0.05936681	0.12673219	0.12348094	0.98242878

	L2p	K2p	K3p	L3p	K4p
(2p$L_\perp$)	0.99999473	0.00076826	0.00292848	-0.00002989	0.00100948
(2p$K_\perp$)	-0.00047300	0.99324024	-0.11076936	0.00597423	0.03416997
(3p$K_\perp$)	-0.00287546	0.11356101	0.98357141	-0.10380163	-0.09438068
(3p$L_\perp$)	-0.00000995	0.01037461	0.08186271	0.97492998	-0.20664535
(4p$K_\perp$)	-0.00130157	-0.02165721	0.11664877	0.19672561	0.97325294

	K3d	L3d	K4d
(3d$K_\perp$)	0.99269887	0.08506565	-0.08551460
(3d$L_\perp$)	-0.08195992	0.99586433	0.03920179
(4d$K_\perp$)	0.08849567	-0.03190680	0.99556538

Neon +6

	K1s	L2s	K2s	K3s	L3s	K4s
(1s$K_\perp$)	0.99768425	0.04774580	0.04808568	-0.00224892	-0.00342115	0.00410591
(2s$L_\perp$)	-0.04972839	0.99789685	0.04072361	0.00688162	-0.00355723	0.00314913
(2s$K_\perp$)	-0.04627627	-0.04340644	0.99215307	0.01506333	-0.07632566	0.07452112
(3s$K_\perp$)	0.00331518	-0.00604524	-0.02149364	0.97959542	-0.17627640	-0.09385775
(3s$L_\perp$)	0.00031385	-0.00058873	0.08243084	0.16427402	0.97387624	-0.13335563
(4s$K_\perp$)	-0.00014051	-0.00076212	-0.06636310	0.11457274	0.12100253	0.98378186

	L2p	K2p	K3p	L3p	K4p
(2p$L_\perp$)	0.99999560	0.00049883	0.00264445	-0.00027280	0.00105827
(2p$K_\perp$)	-0.00025275	0.99404074	-0.10426803	0.00313828	0.03163475
(3p$K_\perp$)	-0.00261897	0.10598544	0.98693193	-0.10090376	-0.06740530
(3p$L_\perp$)	0.00025861	0.01238644	0.08400180	0.97422514	-0.20898687
(4p$K_\perp$)	-0.00120273	-0.02226916	0.08960858	0.20172707	0.97507900

	K3d	L3d	K4d
(3d$K_\perp$)	0.99224537	0.08946254	-0.08628760
(3d$L_\perp$)	-0.08619035	0.99543726	0.04093721
(4d$K_\perp$)	0.08955624	-0.03318260	0.99542884

---

[a] The expansion coefficient for the (K4f) NO is unity because this NO is identical to the (4fK) STAO.

Figure 10. (Continued)

Natural orbital occupation coefficients for separated pair approximations to beryllium-like atomic wavefunctions

NO	Li$^-$	Be	B$^+$	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
Separated pair approximation Φ_2								
K1s	0.99882	0.99938	0.99962	0.99974	0.99982	0.99987	0.99990	0.99992
K2s	-0.02730	-0.02002	-0.01616	-0.01371	-0.01069	-0.00962	-0.00859	-0.00759
K2p	-0.04024	-0.02889	-0.02235	-0.01788	-0.01571	-0.01315	-0.01145	-0.01020
L2s	0.92869	0.94950	0.95695	0.96080	0.96329	0.96492	0.96617	0.96712
L2p	-0.37085	-0.31376	-0.29025	-0.27724	-0.26848	-0.26253	-0.25791	-0.25433
Separated pair approximation Φ_3								
K1s	0.99846	0.99922	0.99953	0.99969	0.99979	0.99984	0.99988	0.99991
K2s	-0.03521	-0.02409	-0.01818	-0.01392	-0.01103	-0.01019	-0.00854	-0.00773
K3s	-0.00360	-0.00247	-0.00205	-0.00189	-0.00168	-0.00156	-0.00140	-0.00127
K2p	-0.04136	-0.03019	-0.02354	-0.01959	-0.01679	-0.01384	-0.01256	-0.01071
K3p	-0.00641	-0.00517	-0.00419	-0.00347	-0.00291	-0.00250	-0.00231	-0.00194
K3d	-0.00859	-0.00660	-0.00534	-0.00447	-0.00382	-0.00345	-0.00309	-0.00281
L2s	0.92864	0.94980	0.95710	0.96104	0.96348	0.96519	0.96637	0.96739
L2p	-0.37098	-0.31286	-0.28976	-0.27642	-0.26779	-0.26154	-0.25717	-0.25328
Separated pair approximation Φ_4								
K1s	0.99846	0.99920	0.99952	0.99968	0.99978	0.99983	0.99987	0.99990
K2s	-0.03529	-0.02432	-0.01842	-0.01493	-0.01228	-0.01060	-0.00910	-0.00817
K3s	-0.00333	-0.00315	-0.00280	-0.00214	-0.00177	-0.00181	-0.00151	-0.00135
K4s	-0.00070	-0.00036	-0.00041	-0.00037	-0.00039	-0.00038	-0.00039	-0.00032
K2p	-0.04103	-0.03021	-0.02354	-0.01919	-0.01610	-0.01384	-0.01235	-0.01071
K3p	-0.00684	-0.00558	-0.00451	-0.00382	-0.00290	-0.00265	-0.00224	-0.00201
K4p	-0.00158	-0.00129	-0.00111	-0.00097	-0.00075	-0.00071	-0.00065	-0.00055
K3d	-0.00903	-0.00695	-0.00579	-0.00483	-0.00415	-0.00374	-0.00316	-0.00281
K4d	-0.00239	-0.00195	-0.00170	-0.00143	-0.00127	-0.00117	-0.00091	-0.00089
K4f	-0.00275	-0.00226	-0.00190	-0.00170	-0.00151	-0.00134	-0.00105	-0.00106
L2s	0.93136	0.95224	0.95817	0.96190	0.96545	0.96597	0.96746	0.96831
L3s	-0.00909	-0.00678	-0.00780	-0.00560	-0.00481	-0.00305	-0.00268	-0.00220
L2p	-0.36369	-0.30469	-0.28560	-0.27297	-0.26017	-0.25835	-0.25281	-0.24954
L3p	-0.00590	-0.00577	-0.00353	-0.00312	-0.00315	-0.00228	-0.00259	-0.00242
L3d	-0.01352	-0.01808	-0.01609	-0.01376	-0.01330	-0.01151	-0.01011	-0.00939

Figure 11. Natural orbital occupation coefficients for separated pair approximations to beryllium-like atomic wavefunctions

Occupation numbers of separated pair approximation Φ_4 for beryllium, nitrogen +3 and neon +6 [a]

	NO	Be	N^{+3}	Ne^{+6}
	K1s	99840.06	99955.68	99974.48
Φ_2	K2s	59.15	15.07	8.27
	K2p	91.26	25.92	15.26
	K3s	0.99	0.31	0.23
Φ_3	K3p	3.11	0.84	0.50
	K3d	4.83	1.72	1.00
	K4s	0.01	0.01	0.02
	K4p	0.17	0.06	0.04
Φ_4	K4d	0.38	0.16	0.08
	K4f	0.51	0.23	0.11
	L2s	90676.10	93210.12	93597.11
Φ_2, Φ_3	L2p	9283.60	6768.88	6391.28
	L3s	4.60	2.31	0.72
Φ_4	L3p	3.33	0.99	0.67
	L3d	32.69	17.69	10.22

[a] The occupation numbers, which are given in units of 10^{-4}, are those of APSG Φ_4. The brackets indicate which orbitals would be included in the APSG's Φ_2, Φ_3 and Φ_4.

Figure 12. Occupation numbers of separated pair approximation Φ_4 for beryllium, nitrogen +3 and neon +6

Comparison between the antisymmetrized product of the first two natural orbitals and the Hartree-Fock wavefunction[a]

APSG	Li^-	Be	B^+	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
Φ_1	0.01743	0.01629	0.02401	0.03817	0.05834	0.08452	0.11655	0.15448
	0.2347%	0.1118%	0.0991%	0.1048%	0.1142%	0.1238%	0.1325%	0.1403%
	0.97213	0.99901	0.99855	0.99768	0.99710	0.99669	0.99636	0.99614
Φ_2	0.00518	0.00177	0.00229	0.00383	0.00546	0.00725	0.00905	0.01100
	0.0697%	0.0121%	0.0095%	0.0105%	0.0107%	0.0106%	0.0103%	0.0100%
	0.96308	0.99876	0.99984	0.99986	0.99982	0.99980	0.99980	0.99977
Φ_3	0.00458	0.00092	0.00080	0.00089	0.00120	0.00133	0.00171	0.00166
	0.0617%	0.0063%	0.0030%	0.0024%	0.0024%	0.0020%	0.0020%	0.0015%
	0.96280	0.99860	0.99974	0.99992	0.99995	0.99995	0.99996	0.99996
Φ_4	0.00445	0.00091	0.00057	0.00059	0.00065	0.00066	0.00107	0.00096
	0.0599%	0.0062%	0.0024%	0.0016%	0.0013%	0.0010%	0.0012%	0.0009%
	0.96305	0.99842	0.99974	0.99993	0.99996	0.99996	0.99997	0.99996

[a] Every entry consists of three numbers. The first line represents the energy difference E(PNO)-E(HF). The second line is the per cent relative deviation 100[E(PNO) - E(HF)]/E(HF). The third line is the overlap between the wavefunctions representing the PNO-AP and the HF-AP.

Figure 13.. Comparison between the antisymmetrized product of the first two natural orbitals and the Hartree-Fock wavefunction

Energies of various separated pair approximations for beryllium-like atoms

Energy	Li^-	Be	B^+	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
$\Delta E(\text{APSG } \Phi_1)$[a]	0.08960	0.11058	0.13539	0.16413	0.19847	0.23802	0.28241	0.33294
$\Delta E(\text{APSG } \Phi_2)$[a]	0.01621 77.54%	0.01922 79.62%	0.02335 79.04%	0.02671 78.80%	0.03036 78.33%	0.03333 78.29%	0.03553 78.58%	0.03828 78.55%
$\Delta E(\text{APSG } \Phi_3)$[a]	0.00914 87.34%	0.01216 87.10%	0.01567 85.93%	0.01786 85.82%	0.02021 85.58%	0.02171 85.86%	0.02233 86.53%	0.02335 86.92%
$\Delta E(\text{APSG } \Phi_4)$[a]	0.00737 89.79%	0.00966 89.76%	0.01280 88.51%	0.01465 88.37%	0.01654 88.20%	0.01776 88.43%	0.01834 88.94%	0.01919 89.25%
$\Delta E(\text{SP})$[b]	0.00594 91.77%	0.00808 91.43%	0.01100 90.12%	0.01280 89.84%	0.01449 89.66%	0.01566 89.80%	0.01623 90.22%	0.01705 90.45%
$\Delta E(\text{corr.})$[c]	-0.07217	-0.09429	-0.11138	-0.12596	-0.14013	-0.15350	-0.16586	-0.17846
$E(\text{HF})$[d]	-7.42823	-14.57302	-24.23758	-36.40850	-51.08231	-68.25771	-87.93404	-110.1110
$E(\text{exact})$[e, f]	-7.50040	-14.66731	-24.34896	-36.53446	-51.22244	-68.41121	-88.09990	-110.28946
$E(\text{rel.})$[e]		0.000165	0.000511	0.001553	0.003668	0.007378	0.013294	
I_1[e]		-0.342622	-0.924504	-1.759554	-2.847142	-4.186058	-5.775691	
I_2[e]		-0.669283	-1.393994	-2.370213	-3.597518	-5.075930	-6.805794	
E^{++}[e]		-13.655566	-22.030972	-32.406247	-44.781445	-59.156595	-75.531712	
Results of other calculations								
$\Delta E(\text{LS})$[g, h]		0.0674	0.0784	0.0945	0.1167	0.1447	0.1780	0.2178
$\Delta E(\text{MS})$[g, i]	0.050	0.056	0.067	0.082	0.104	0.131		
$\Delta E(\text{W})$[g, j]		0.05079	0.05316	0.05429	0.05557	0.05640	0.05641	0.05680

[a] $\Delta E(\text{APSG } \Phi_i) = E(\text{APSG } \Phi_i) - E(\text{exact})$. Also given is the per cent correlation energy recovered, i.e., $100\{E(\text{APSG } \Phi_i) - E(\text{HF})\}/\{E(\text{exact}) - E(\text{HF})\}$.

[b] $\Delta E(\text{SP})$ = estimated limit of separated pair approximation.

[c] $\Delta E(\text{corr.}) = E(\text{exact}) - E(\text{HF})$.

[d] C. C. J. Roothaan, L. M. Sachs and A. M. Weiss, Rev. Mod. Phys. 32, 179 (1960).

[e] $E(\text{exact}) = E^{++} + I_1 + I_2 + E(\text{rel.})$ = exact non-relativistic energy corrected to infinite nuclear mass.

[f] The values for lithium -1 and neon +6 are obtained by extrapolation.

[g] $\Delta E(\cdots) = E(\cdots) - E(\text{exact})$.

[h] E(LS) = energies calculated by J. Linderberg and H. Shull, J. Mol. Spect. 5, 1 (1960).

[i] E(MS) = energies calculated by R. McWeeny and B. T. Sutcliffe, Proc. Roy. Soc. 273, 103 (1963).

[j] E(W) = energies calculated by R. E. Watson, Ann. Phys. 13, 250 (1961).

Figure 14. Energies of various separated pair approximations for beryllium-like atoms

K-geminal defect of two-electron systems

Energy[a]	Li^+	Be^{+2}	B^{+3}	C^{+4}	N^{+5}	O^{+6}	F^{+7}	Ne^{+8}
E_2^{++}	-7.26930	-13.64527	-22.02066	-32.39573	-44.77071	-59.14556	-75.52048	-93.89532
D_2^{++}	-0.01061	-0.01030	-0.01031	-0.01052	-0.01074	-0.01104	-0.01123	-0.01149
E_3^{++}	-7.27671	-13.65224	-22.02740	-32.40248	-44.77745	-59.15241	-75.52749	-93.90245
D_3^{++}	-0.00320	-0.00333	-0.00357	-0.00377	-0.00400	-0.00419	-0.00422	-0.00436
E_4^{++}	-7.27848	-13.65399	-22.02917	-32.40440	-44.77940	-59.15450	-75.52960	-93.90467
D_4^{++}	-0.00143	-0.00158	-0.00180	-0.00185	-0.00205	-0.00210	-0.00211	-0.00214
E^{++}	-7.27991	-13.65557	-22.03097	-32.40625	-44.78145	-59.15660	-75.53171	-93.90681

[a] E_i^{++} = energy calculated using the approximation Φ_i^{++}.

$E^{++} = E_i^{++} + D_i^{++}$ = exact two-electron energy.

Figure 15. K-geminal defect of two-electron systems

Energy analysis of separated pair approximations for lithium -1

Contributions	APSG Φ_4		APSG Φ_3		APSG Φ_2	
ε(K1s, K1s)		-7.23561		-7.23565		-7.23521
$\Delta\varepsilon$(K1s, K2s)	-0.01385		-0.01378		-0.01234	
$\Delta\varepsilon$(K1s, K3s)	-0.00075		-0.00079			
$\Delta\varepsilon$(K1s, K4s)	-0.00001					
$\Delta\varepsilon$(K1s, K2p)	-0.02051		-0.02066		-0.02108	
$\Delta\varepsilon$(K1s, K3p)	-0.00204		-0.00211			
$\Delta\varepsilon$(K1s, K4p)	-0.00031					
$\Delta\varepsilon$(K1s, K3d)	-0.00244		-0.00247			
$\Delta\varepsilon$(K1s, K4d)	-0.00051					
$\Delta\varepsilon$(K1s, K4f)	-0.00056					
$\Delta\varepsilon$(K1s)		-0.04098		-0.03981		-0.03342
$\Delta\varepsilon$(K, others)		-0.00028		-0.00013		-0.00008
ΔE(K)		-0.04126		-0.03994		-0.03350
E(K)		-7.27687		-7.27559		-7.26871
ε(L2s, L2s)		-1.18767		-1.18744		-1.18740
$\Delta\varepsilon$(L2s, L3s)	-0.00019					
$\Delta\varepsilon$(L2s, L2p)	-0.02342		-0.02384		-0.02383	
$\Delta\varepsilon$(L2s, L3p)	-0.00011					
$\Delta\varepsilon$(L2s, L3d)	-0.00053					
$\Delta\varepsilon$(L2s)		-0.02425		-0.02384		-0.02383
$\Delta\varepsilon$(L2p, L2p)	0.02226		0.02302		0.02280	
$\Delta\varepsilon$(L2p, L2s)	-0.02342		-0.02384		-0.02383	
$\Delta\varepsilon$(L2p, L3s)	0.00006					
$\Delta\varepsilon$(L2p, L3p)	0.00008					
$\Delta\varepsilon$(L2p, L3d)	0.00043					
$\Delta\varepsilon$(L2p)		-0.00059		-0.00082		-0.00103
$\Delta\varepsilon$(L, others)		-0.00010		0.00000		0.00000
ΔE(L)		-0.02494		-0.02466		-0.02486
E(L)		-1.21261		-1.21210		-1.21226
$\mathcal{I}$(K1s, L2s)		0.99950		0.99944		0.99956
$\Delta\mathcal{I}$(K1s, L2p)	-0.00300		-0.00298		-0.00277	
$\Delta\mathcal{I}$(others)	-0.00005		-0.00003		-0.00001	
ΔI(K, L)		-0.00305		-0.00301		-0.00278
I(K, L)		0.99645		0.99643		0.99678
E(PNO)		-7.42378		-7.42365		-7.42305
E-E(PNO)		-0.06925		-0.06761		-0.06114
E=E(K)+E(L)+I(K, L)		-7.49303		-7.49126		-7.48419

Figure 16. Energy analysis of separated pair approximations for lithium -1

Energy analysis of separated pair approximations for beryllium

Contributions	APSG Φ_4		APSG Φ_3		APSG Φ_2	
ε(K1s, K1s)		-13.60677		-13.60721		-13.60720
$\Delta\varepsilon$(K1s, K2s)	-0.01291		-0.01257		-0.01183	
$\Delta\varepsilon$(K1s, K3s)	-0.00082		-0.00078			
$\Delta\varepsilon$(K1s, K4s)	-0.00006					
$\Delta\varepsilon$(K1s, K2p)	-0.02076		-0.02055		-0.02089	
$\Delta\varepsilon$(K1s, K3p)	-0.00209		-0.00221			
$\Delta\varepsilon$(K1s, K4p)	-0.00036					
$\Delta\varepsilon$(K1s, K3d)	-0.00252		-0.00263			
$\Delta\varepsilon$(K1s, K4d)	-0.00055					
$\Delta\varepsilon$(K1s, K4f)	-0.00061					
$\Delta\varepsilon$(K1s)		-0.04068		-0.03874		-0.03272
$\Delta\varepsilon$(K, *others*)		0.00020		-0.00007		-0.00001
ΔE(K)		-0.04048		-0.03881		-0.03273
E(K)		-13.64725		-13.64602		-13.63993
ε(L2s, L2s)		-2.85549		-2.85357		-2.85596
$\Delta\varepsilon$(L2s, L3s)	-0.00023					
$\Delta\varepsilon$(L2s, L2p)	-0.03905		-0.03985		-0.03973	
$\Delta\varepsilon$(L2s, L3p)	-0.00019					
$\Delta\varepsilon$(L2s, L3d)	-0.00128					
$\Delta\varepsilon$(L2s)		-0.04075		-0.03985		-0.03973
$\Delta\varepsilon$(L2p, L2p)	0.02945		0.03089		0.03154	
$\Delta\varepsilon$(L2p, L2s)	-0.03905		-0.03985		-0.03973	
$\Delta\varepsilon$(L2p, L3s)	0.00006					
$\Delta\varepsilon$(L2p, L3p)	0.00014					
$\Delta\varepsilon$(L2p, L3d)	0.00085					
$\Delta\varepsilon$(L2p)		-0.00855		-0.00896		-0.00819
$\Delta\varepsilon$(L, others)		0.00002		0.00000		0.00000
ΔE(L)		-0.04928		-0.04881		-0.04792
E(L)		-2.90477		-2.90238		-2.90388
$\mathcal{I}$(K1s, L2s)		1.89015		1.88868		1.89191
$\Delta\mathcal{I}$(K1s, L2p)	0.00439		0.00463		0.00384	
$\Delta\mathcal{I}$(others)	-0.00017		-0.00006		-0.00003	
ΔI(K, L)		0.00422		0.00457		0.00381
I(K, L)		1.89437		1.89325		1.89572
E(PNO)		-14.57211		-14.57210		-14.57125
E-E(PNO)		-0.08554		-0.08305		-0.07684
E=E(K)+E(L)+I(K, L)		-14.65765		-14.65515		-14.64809

Figure 17. Energy analysis of separated pair approximations for beryllium

Energy analysis of separated pair approximations for boron +1

Contributions	APSG Φ_4		APSG Φ_3		APSG Φ_2	
$\varepsilon(K1s, K1s)$		-21.97820		-21.97860		-21.97876
$\Delta\varepsilon(K1s, K2s)$	-0.01186		-0.01169		-0.01152	
$\Delta\varepsilon(K1s, K3s)$	-0.00095		-0.00081			
$\Delta\varepsilon(K1s, K4s)$	-0.00008					
$\Delta\varepsilon(K1s, K2p)$	-0.02034		-0.02032		-0.02045	
$\Delta\varepsilon(K1s, K3p)$	-0.00223		-0.00222			
$\Delta\varepsilon(K1s, K4p)$	-0.00034					
$\Delta\varepsilon(K1s, K3d)$	-0.00271		-0.00271			
$\Delta\varepsilon(K1s, K4d)$	-0.00057					
$\Delta\varepsilon(K1s, K4f)$	-0.00064					
$\Delta\varepsilon(K1s)$		-0.03972		-0.03775		-0.03197
$\Delta\varepsilon(K, \text{others})$		0.00028		0.00001		0.00000
$\Delta E(K)$		-0.03944		-0.03774		-0.03197
$E(K)$		-22.01764		-22.01634		-22.01073
$\varepsilon(L2s, L2s)$		-4.98125		-4.98204		-4.97780
$\Delta\varepsilon(L2s, L3s)$	-0.00032					
$\Delta\varepsilon(L2s, L2p)$	-0.05307		-0.05377		-0.05339	
$\Delta\varepsilon(L2s, L3p)$	-0.00015					
$\Delta\varepsilon(L2s, L3d)$	-0.00161					
$\Delta\varepsilon(L2s)$		-0.05515		-0.05377		-0.05339
$\Delta\varepsilon(L2p, L2p)$	0.03655		0.03761		0.03750	
$\Delta\varepsilon(L2p, L2s)$	-0.05307		-0.05377		-0.05339	
$\Delta\varepsilon(L2p, L3s)$	0.00009					
$\Delta\varepsilon(L2p, L3p)$	0.00008					
$\Delta\varepsilon(L2p, L3d)$	0.00099					
$\Delta\varepsilon(L2p)$		-0.01536		-0.01616		-0.01589
$\Delta\varepsilon(L, \text{others})$		0.00012		0.00000		0.00000
$\Delta E(L)$		-0.07039		-0.06993		-0.06928
$E(L)$		-5.05164		-5.05197		-5.04708
$\mathcal{I}(K1s, L2s)$		2.72244		2.72386		2.72127
$\Delta\mathcal{I}(K1s, L2p)$	0.01093		0.01123		0.01096	
$\Delta\mathcal{I}(\text{others})$	-0.00025		-0.00007		-0.00003	
$\Delta I(K, L)$		0.01068		0.01116		0.01093
$I(K, L)$		2.73312		2.73502		2.73220
$E(PNO)$		-24.23701		-24.23678		-24.23529
$E-E(PNO)$		-0.09915		-0.09651		-0.09032
$E=E(K)+E(L)+I(K, L)$		-24.33616		-24.33329		-24.32561

Figure 18. Energy analysis of separated pair approximations for boron +1

Energy analysis of separated pair approximations for carbon +2

Contributions	APSG Φ_4		APSG Φ_3		APSG Φ_2	
ε(K1s, K1s)		-32.35049		-32.35093		-32.35079
$\Delta\varepsilon$(K1s, K2s)	-0.01128		-0.01050		-0.01134	
$\Delta\varepsilon$(K1s, K3s)	-0.00087		-0.00088			
$\Delta\varepsilon$(K1s, K4s)	-0.00008					
$\Delta\varepsilon$(K1s, K2p)	-0.02004		-0.02042		-0.01988	
$\Delta\varepsilon$(K1s, K3p)	-0.00225		-0.00223			
$\Delta\varepsilon$(K1s, K4p)	-0.00036					
$\Delta\varepsilon$(K1s, K3d)	-0.00275		-0.00273			
$\Delta\varepsilon$(K1s, K4d)	-0.00057					
$\Delta\varepsilon$(K1s, K4f)	-0.00068					
$\Delta\varepsilon$(K1s)		-0.03888		-0.03676		-0.03122
$\Delta\varepsilon$(K, others)		0.00029		0.00001		0.00004
ΔE(K)		-0.03859		-0.03675		-0.03118
E(K)		-32.38908		-32.38768		-32.38197
ε(L2s, L2s)		-7.59180		-7.59274		-7.59365
$\Delta\varepsilon$(L2s, L3s)	-0.00026					
$\Delta\varepsilon$(L2s, L2p)	-0.06589		-0.06664		-0.06632	
$\Delta\varepsilon$(L2s, L3p)	-0.00016					
$\Delta\varepsilon$(L2s, L3d)	-0.00178					
$\Delta\varepsilon$(L2s)		-0.06809		-0.06664		-0.06632
$\Delta\varepsilon$(L2p, L2p)	0.04155		0.04256		0.04308	
$\Delta\varepsilon$(L2p, L2s)	-0.06589		-0.06664		-0.06632	
$\Delta\varepsilon$(L2p, L3s)	0.00007					
$\Delta\varepsilon$(L2p, L3p)	0.00008					
$\Delta\varepsilon$(L2p, L3d)	0.00102					
$\Delta\varepsilon$(L2p)		-0.02317		-0.02408		-0.02324
$\Delta\varepsilon$(L, others)		0.00012		0.00000		0.00000
ΔE(L)		-0.09114		-0.09072		-0.08956
E(L)		-7.68294		-7.68346		-7.68321
$\mathcal{I}$(K1s, L2s)		3.53438		3.53606		3.53977
$\Delta\mathcal{I}$(K1s, L2p)	0.01807		0.01855		0.01770	
$\Delta\mathcal{I}$(others)	-0.00024		-0.00007		-0.00004	
ΔI(K, L)		0.01783		0.01848		0.01766
I(K, L)		3.55221		3.55454		3.55743
E(PNO)		-36.40791		-36.40761		-36.40467
E-E(PNO)		-0.11190		-0.10899		-0.10308
E=E(K)+E(L)+I(K, L)		-36.51981		-36.51660		-36.50775

Figure 19. Energy analysis of separated pair approximations for carbon +2

Energy analysis of separated pair approximations for nitrogen +3

Contributions	APSG Φ_4		APSG Φ_3		APSG Φ_2	
ε(K1s, K1s)		-44.72223		-44.72360		-44.72369
$\Delta\varepsilon$(K1s, K2s)	-0.01072		-0.00965		-0.01007	
$\Delta\varepsilon$(K1s, K3s)	-0.00085		-0.00089			
$\Delta\varepsilon$(K1s, K4s)	-0.00010					
$\Delta\varepsilon$(K1s, K2p)	-0.01977		-0.02050		-0.02046	
$\Delta\varepsilon$(K1s, K3p)	-0.00205		-0.00223			
$\Delta\varepsilon$(K1s, K4p)	-0.00030					
$\Delta\varepsilon$(K1s, K3d)	-0.00276		-0.00273			
$\Delta\varepsilon$(K1s, K4d)	-0.00059					
$\Delta\varepsilon$(K1s, K4f)	-0.00070					
$\Delta\varepsilon$(K1s)		-0.03784		-0.03600		-0.03053
$\Delta\varepsilon$(K, others)		-0.00012		0.00002		0.00006
ΔE(K)		-0.03796		-0.03598		-0.03047
E(K)		-44.76019		-44.75958		-44.75416
ε(L2s, L2s)		-10.69690		-10.69730		-10.69650
$\Delta\varepsilon$(L2s, L3s)	-0.00023		-0.07897		-0.07860	
$\Delta\varepsilon$(L2s, L2p)	-0.07696					
$\Delta\varepsilon$(L2s, L3p)	-0.00020					
$\Delta\varepsilon$(L2s, L3d)	-0.00211					
$\Delta\varepsilon$(L2s)		-0.07950		-0.07897		-0.07860
$\Delta\varepsilon$(L2p, L2p)	0.04480		0.04733		0.04737	
$\Delta\varepsilon$(L2p, L2s)	-0.07696		-0.07897		-0.07860	
$\Delta\varepsilon$(L2p, L3s)	0.00006					
$\Delta\varepsilon$(L2p, L3p)	0.00009					
$\Delta\varepsilon$(L2p, L3d)	0.00114					
$\Delta\varepsilon$(L2p)		-0.03087		-0.03164		-0.03123
$\Delta\varepsilon$(L, others)		0.00023		0.00000		0.00000
ΔE(L)		-0.11014		-0.11061		-0.10983
E(L)		-10.80704		-10.80791		-10.80633
$\mathcal{I}$(K1s, L2s)		4.33747		4.33979		4.34334
$\Delta\mathcal{I}$(K1s, L2p)	0.02412		0.02553		0.02510	
$\Delta\mathcal{I}$(others)	-0.00026		-0.00006		-0.00003	
ΔI(K, L)		0.02386		0.02547		0.02507
I(K, L)		4.36133		4.36526		4.36841
E(PNO)		-51.08166		-51.08111		-51.07685
E-E(PNO)		-0.12424		-0.12112		-0.11523
E=E(K)+E(L)+I(K, L)		-51.20590		-51.20223		-51.19208

Figure 20. Energy analysis of separated pair approximations for nitrogen +3

Energy analysis of separated pair approximations for oxygen +4

Contributions	APSG Φ_4		APSG Φ_3		APSG Φ_2	
$\varepsilon(K1s, K1s)$		-59.09645		-59.09689		-59.09693
$\Delta\varepsilon(K1s, K2s)$	-0.01056		-0.01023		-0.01005	
$\Delta\varepsilon(K1s, K3s)$	-0.00094		-0.00089			
$\Delta\varepsilon(K1s, K4s)$	-0.00012					
$\Delta\varepsilon(K1s, K2p)$	-0.01953		-0.01940		-0.01987	
$\Delta\varepsilon(K1s, K3p)$	-0.00214		-0.00218			
$\Delta\varepsilon(K1s, K4p)$	-0.00033					
$\Delta\varepsilon(K1s, K3d)$	-0.00283		-0.00284			
$\Delta\varepsilon(K1s, K4d)$	-0.00062					
$\Delta\varepsilon(K1s, K4f)$	-0.00071					
$\Delta\varepsilon(K1s)$		-0.03778		-0.03554		-0.02992
$\Delta\varepsilon(K, \text{others})$		0.00038		0.00020		0.00003
$\Delta E(K)$		-0.03740		-0.03534		-0.02989
$E(K)$		-59.13385		-59.13223		-59.12682
$\varepsilon(L2s, L2s)$		-14.29999		-14.30172		-14.30388
$\Delta\varepsilon(L2s, L3s)$	-0.00016					
$\Delta\varepsilon(L2s, L2p)$	-0.08999		-0.09102		-0.09075	
$\Delta\varepsilon(L2s, L3p)$	-0.00016					
$\Delta\varepsilon(L2s, L3d)$	-0.00215					
$\Delta\varepsilon(L2s)$		-0.09246		-0.09102		-0.09075
$\Delta\varepsilon(L2p, L2p)$	0.04980		0.05101		0.05244	
$\Delta\varepsilon(L2p, L2s)$	-0.08999		-0.09102		-0.09075	
$\Delta\varepsilon(L2p, L3s)$	0.00004					
$\Delta\varepsilon(L2p, L3p)$	0.00008					
$\Delta\varepsilon(L2p, L3d)$	0.00114					
$\Delta\varepsilon(L2p)$		-0.03893		-0.04001		-0.03831
$\Delta\varepsilon(L, \text{others})$		0.00014		0.00000		0.00000
$\Delta E(L)$		-0.13125		-0.13103		-0.12906
$E(L)$		-14.43124		-14.43275		-14.43294
$\mathcal{J}(K1s, L2s)$		5.13939		5.14223		5.15035
$\Delta\mathcal{J}(K1s, L2p)$	0.03248		0.03332		0.03157	
$\Delta\mathcal{J}(\text{others})$	-0.00023		-0.00007		-0.00004	
$\Delta I(K, L)$		0.03225		0.03325		0.03153
$I(K, L)$		5.17164		5.17548		5.18188
$E(PNO)$		-68.25705		-68.25638		-68.25046
$E-E(PNO)$		-0.13640		-0.13312		-0.12742
$E=E(K)+E(L)+I(K, L)$		-68.39345		-68.38950		-68.37788

Figure 21. Energy analysis of separated pair approximations for oxygen +4

Energy analysis of separated pair approximations for fluorine +5

Contributions	APSG Φ_4		APSG Φ_3		APSG Φ_2	
ε(K1s, K1s)		-75.47009		-75.47045		-75.47030
$\Delta\varepsilon$(K1s, K2s)	-0.01014		-0.00949		-0.00997	
$\Delta\varepsilon$(K1s, K3s)	-0.00090		-0.00091			
$\Delta\varepsilon$(K1s, K4s)	-0.00013					
$\Delta\varepsilon$(K1s, K2p)	-0.01965		-0.01984		-0.01944	
$\Delta\varepsilon$(K1s, K3p)	-0.00198		-0.00224			
$\Delta\varepsilon$(K1s, K4p)	-0.00036					
$\Delta\varepsilon$(K1s, K3d)	-0.00272		-0.00285			
$\Delta\varepsilon$(K1s, K4d)	-0.00054					
$\Delta\varepsilon$(K1s, K4f)	-0.00062					
$\Delta\varepsilon$(K1s)		-0.03704		-0.03533		-0.02941
$\Delta\varepsilon$(K, others)		0.00007		0.00041		0.00005
ΔE(K)		-0.03697		-0.03492		-0.02936
E(K)		-75.50706		-75.50537		-75.49966
ε(L2s, L2s)		-18.40667		-18.40711		-18.40545
$\Delta\varepsilon$(L2s, L3s)	-0.00015					
$\Delta\varepsilon$(L2s, L2p)	-0.10137		-0.10298		-0.10264	
$\Delta\varepsilon$(L2s, L3p)	-0.00021					
$\Delta\varepsilon$(L2s, L3d)	-0.00218					
$\Delta\varepsilon$(L2s)		-0.10391		-0.10298		-0.10264
$\Delta\varepsilon$(L2p, L2p)	0.05477		0.05680		0.05447	
$\Delta\varepsilon$(L2p, L2s)	-0.10137		-0.10298		-0.10264	
$\Delta\varepsilon$(L2p, L3s)	0.00004					
$\Delta\varepsilon$(L2p, L3p)	0.00010					
$\Delta\varepsilon$(L2p, L3d)	0.00113					
$\Delta\varepsilon$(L2p)		-0.04533		-0.04618		-0.04817
$\Delta\varepsilon$(L, others)		0.00012		0.00000		0.00000
ΔE(L)		-0.14912		-0.14916		-0.15081
E(L)		-18.55579		-18.55627		-18.55626
$\mathcal{J}$(K1s, L2s)		5.94379		5.94523		5.95076
$\Delta\mathcal{J}$(K1s, L2p)	0.03770		0.03889		0.04083	
$\Delta\mathcal{J}$(others)	-0.00020		-0.00005		-0.00004	
ΔI(K, L)		0.03750		0.03884		0.04079
I(K, L)		5.98129		5.98407		5.99155
E(PNO)		-87.93297		-87.93233		-87.92499
E-E(PNO)		-0.14859		-0.14524		-0.13938
E=E(K)+E(L)+I(K, L)		-88.08156		-88.07757		-88.06437

Figure 22. Energy analysis of separated pair approximations for fluorine +5

Energy analysis of separated pair approximations for neon +6

Contributions	APSG Φ_4		APSG Φ_3		APSG Φ_2	
ε(K1s, K1s)		-93.84371		-93.84472		-93.84426
Δε(K1s, K2s)	-0.01016		-0.00977		-0.00961	
Δε(K1s, K3s)	-0.00087		-0.00086			
Δε(K1s, K4s)	-0.00012					
Δε(K1s, K2p)	-0.01900		-0.01903		-0.01936	
Δε(K1s, K3p)	-0.00205		-0.00208			
Δε(K1s, K4p)	-0.00031					
Δε(K1s, K3d)	-0.00268		-0.00288			
Δε(K1s, K4d)	-0.00059					
Δε(K1s, K4f)	-0.00069					
Δε(K1s)		-0.03647		-0.03462		-0.02897
Δε(K, others)		-0.00016		0.00005		0.00001
ΔE(K)		-0.03663		-0.03457		-0.02896
E(K)		-93.88034		-93.87929		-93.87322
ε(L2s, L2s)		-22.99596		-22.99404		-23.00265
Δε(L2s, L3s)	-0.00013					
Δε(L2s, L2p)	-0.11282		-0.11432		-0.11427	
Δε(L2s, L3p)	-0.00022					
Δε(L2s, L3d)	-0.00230					
Δε(L2s)		-0.11547		-0.11432		-0.11427
Δε(L2p, L2p)	0.05757		0.05904		0.05903	
Δε(L2p, L2s)	-0.11282		-0.11432		-0.11427	
Δε(L2p, L3s)	0.00003					
Δε(L2p, L3p)	0.00010					
Δε(L2p, L3d)	0.00116					
Δε(L2p)		-0.05396		-0.05528		-0.05524
Δε(L, others)		0.00016		0.00000		0.00000
ΔE(L)		-0.16927		-0.16960		-0.16951
E(L)		-23.16523		-23.16364		-23.17216
$\mathcal{I}$(K1s, L2s)		6.72963		6.72942		6.74691
Δ$\mathcal{I}$(K1s, L2p)	0.04586		0.04743		0.04732	
Δ$\mathcal{I}$(others)	-0.00019		-0.00003		-0.00003	
ΔI(K, L)		0.04567		0.04740		0.04729
I(K, L)		6.77530		6.77682		6.79420
E(PNO)		-110.11004		-110.10934		-110.10000
E-E(PNO)		-0.16023		-0.15677		-0.15118
E=E(K)+E(L)+I(K, L)		-110.27027		-110.26611		-110.25118

Figure 23. Energy analysis of separated pair approximations for neon +6

Analysis of electronic energy of Ebbing and Henderson's separated pair approximation for lithium hydride[a]

Contributions	Values	
$\varepsilon(I\chi 1, I\chi 1)$		-7.89420
$\Delta\varepsilon(I\chi 1, I\chi 2)$	-0.01283	
$\Delta\varepsilon(I\chi 1, I\chi 3)$	-0.00554	
$\Delta\varepsilon(I\chi 1, I\chi 4)$	-0.00004	
$\Delta\varepsilon(I\chi 1)$		-0.01841
$\Delta\varepsilon(I, \text{others})$		0.00030
$\Delta E(I)$		-0.01811
$E(I)$		-7.91231
$\varepsilon(O\chi 1, O\chi 1)$		-2.46863
$\Delta\varepsilon(O\chi 1, O\chi 2)$	-0.01245	
$\Delta\varepsilon(O\chi 1, O\chi 3)$	-0.00530	
$\Delta\varepsilon(O\chi 1)$		-0.01775
$\Delta\varepsilon(O\chi 2, O\chi 2)$	0.01175	
$\Delta\varepsilon(O\chi 2, O\chi 1)$	-0.01245	
$\Delta\varepsilon(O\chi 2, O\chi 3)$	0.00014	
$\Delta\varepsilon(O\chi 2)$		-0.00056
$\Delta\varepsilon(O\chi 3, O\chi 3)$	0.00635	
$\Delta\varepsilon(O\chi 3, O\chi 1)$	-0.00530	
$\Delta\varepsilon(O\chi 3, O\chi 2)$	0.00015	
$\Delta\varepsilon(O\chi 3)$		0.00120
$\Delta\varepsilon(O, \text{others})$		0.00000
$\Delta E(O)$		-0.01711
$E(O)$		-2.48574
$\mathcal{I}(I\chi 1, O\chi 1)$		1.38115
$\Delta\mathcal{I}(I\chi 1, O\chi 2)$	0.00032	
$\Delta\mathcal{I}(I\chi 1, O\chi 3)$	-0.00127	
$\Delta\mathcal{I}(I\chi 2, O\chi 1)$	-0.00010	
$\Delta\mathcal{I}(\text{others})$	0.00002	
$\Delta I(I, O)$		-0.00103
$I(I, O)$		1.38012
$E(\text{PNO})$		-8.98168
$E-E(\text{PNO})$		-0.03625
$E=E(I)+E(O)+I(I, O)$		-9.01793

[a] Relation to the notation of D. D. Ebbing and R. C. Henderson [J. Chem. Phys. **42**, 2225 (1965)]: $(I\chi j) \equiv \chi_j^I$, $(O\chi j) \equiv \chi_j^O$.

Figure 24. Analysis of electronic energy of Ebbing and Henderson's separated pair approximation for lithium hydride

Comparison of shell correlations for the beryllium atom [a]

Source	K-shell [a]	L-shell [a]	Intrashell total [a]
Kelly [b]	-0.04212	-0.04488	-0.08700
Tuan, Sinanoğlu [c]	-0.04395	-0.04392	-0.08787
Geller, et. al. [d]	-0.042083	-0.044381	-0.086464
APSG Φ_4	-0.04048	-0.04489	-0.08537
APSG Φ_{SP} [e]	-0.04206	-0.04489	-0.08695

[a] Listed are $E_{corr.}(1s^2)$ and $E_{corr.}(2s^2)$ for the first three authors, and $\Delta\tilde{E}(K)$ and $\Delta\tilde{E}(L)$ for the present work. Thus for the first three authors the intrashell total represents the energy lowering beyond the Hartree-Fock energy, but for the present work it represents the lowering beyond the energy calculated from the antisymmetrized product of the principal NO's. Since the latter lies 0.00091 a.u. above the Hartree-Fock energy, the sum of -0.03695 a.u. given for APSG Φ_{SP} would correspond to a correlation energy recovered of -0.08604 a.u.. To this must be added the contribution $\Delta\tilde{I}(K, L) = -0.00017$ to obtain the total correlation energy recovered of -0.08621 a.u. for Φ_{SP}.

[b] H. P. Kelly, Phys. Rev. 131, 684 (1963); ibid. 136, B896 (1964).

[c] D. F. Tuan and O. Sinanoğlu, J. Chem. Phys. 41, 2677 (1964). The accuracy of these numbers is questioned by GTL, ref. d. Conversion to eV was made by M. Geller, et. al., ref. d.

[d] M. Geller, H. S. Taylor and H. B. Levine, J. Chem. Phys. 43, 1727 (1965).

[e] The K-shell energy for APSG Φ_{SP} differs from that for APSG Φ_4 as discussed in the section on the K-shell correction.

Figure 25. Comparison of shell correlations for the beryllium atom

Wavefunction and energies of various pair approximations containing interelectronic distances for beryllium

Calculation	1		2		3	
STAO exponents in X_K and X_L	Fixed		Varied		Varied	
Occupation coefficients in APSG Φ_i	Fixed		Fixed		Varied	
	Correlated pair approximation APG $\tilde{\Phi}_1$					
	a	ζ	a	ζ	a	ζ
APSG Φ_1	0.45679		0.15846			
X_K	0.10205	3.685	0.13787	3.839		
X_L	0.47220	0.956	0.72858	1.126		
E(APG $\tilde{\Phi}_1$)	-14.60384		-14.63094			
E(APG $\tilde{\Phi}_1$)-E(APSG Φ_1)	-0.04711		-0.07421			
E(APSG Φ_2)-E(APSG Φ_1)	-0.09136		-0.09136			
	Correlated pair approximation APG $\tilde{\Phi}_2$					
	a	ζ	a	ζ	a	ζ
APSG Φ_2	0.98029		0.74513		0.72954	
X_K	0.02207	3.405	0.05784	3.895	0.07600	3.905
X_L	0.00149	0.993	0.20703	1.123	0.20740	1.123
E(APG $\tilde{\Phi}_2$)	-14.64934		-14.65259		-14.65357	
E(APG $\tilde{\Phi}_2$)-E(APSG Φ_2)	-0.00125		-0.00450		-0.00548	
E(APSG Φ_3)-E(APSG Φ_2)	-0.00706		-0.00706		-0.00706	

a ≡ coefficients of Φ_i, X_K and X_L. ζ ≡ orbital exponents in X_K and X_L.

Figure 26. Wavefunction and energies of various pair approximations containing interelectronic distances for beryllium

Classification of essential augmented separated pair configurations according to natural orbital geminals[a]

Class 2b

Factorization used in calculation[b]

Geminals	(K1s, L2s)
(K2p, L2p)	3, 8
(K3p, L2p)	14
(K2p, L3p)	4, 11
(K3p, L3p)	17
(K3d, L3d)	21, 25
(K4d, L3d)	28

Alternative factorization[c]

Geminals	(L2s, L2p)	(L2s, L3p)	(L2s, L3d)
(K1s, K2p)	3, 8	4, 11	f
(K1s, K3p)	14	17	f
(K1s, K3d)	f	f	21, 25
(K1s, K4d)	f	f	28

Class 3

Geminals	(K1s, L2s)	(K2s, L2s)	(K2p, L2p)
(K1s, K1s)	d	g	26
(K2s, K2s)	2	d	g
(K3s, K3s)	16	g	g
(K1s, K2s)	e	e	15
(K2s, K3s)	19	g	g
(K2p, K2p)	6	g	d
(K3p, K3p)	23	g	g
(K2p, K3p)	5, 7	g	g
(K2p, K4p)	20	g	g
(K3p, K4p)	18	g	g
(K3d, K3d)	27	g	g
(K3d, K4d)	13, 24	g	g
(L2s, L2s)	d	d	1
(L2p, L2p)	10	9	d

Class 4

Geminals	(K2s, K2s)
(K1s, K1s)	12

Geminals	(L2p, L2p)
(L2s, L2s)	22

---

[a] Each number corresponds to one ASPC and indicates the order of importance as exhibited in the energy analysis of ASPE Ψ_4.

[b] Both geminals have angular momentum $L = 0$.

[c] One geminal contains only K-shell orbitals and the other contains only L-shell orbitals.

[d] ASPC vanishes because of antisymmetry.

[e] ASPC is equivalent to an ASPC listed elsewhere.

[f] Total angular momentum $L \neq 0$.

[g] ASPC contributes less than 10^{-5} a.u. to the total energy lowering beyond the separated pair approximation.

Figure 27. Classification of essential augmented separated pair configurations according to natural orbital geminals

Energies of various augmented separated pair exoansions for beryllium-like atoms

Energy[a]	Li^-	Be	B^+	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
$\Delta E(HF)$[b]	0.07217	0.09429	0.11138	0.12596	0.14013	0.15350	0.16586	0.17846
$\Delta E(APSG\ \Phi_2)$[c]	0.01621	0.01922	0.02335	0.02671	0.03036	0.03333	0.03553	0.03828
$\Delta E(ASPE\ \Psi_2)$[d]	0.01537	0.01645	0.01895	0.02100	0.02362	0.02587	0.02737	0.02973
	78.70%	82.55%	82.99%	83.33%	83.14%	83.15%	83.50%	83.34%
$\Delta E(APSG\ \Phi_3)$[c]	0.00914	0.01216	0.01567	0.01786	0.02021	0.02171	0.02233	0.02335
$\Delta E(ASPE\ \Psi_3)$[d]	0.00808	0.00874	0.01032	0.01103	0.01224	0.01299	0.01288	0.01359
	88.80%	90.73%	90.73%	91.24%	91.27%	91.54%	92.24%	92.39%
$\Delta E(APSG\ \Phi_4)$[c]	0.00737	0.00966	0.01280	0.01465	0.01654	0.01776	0.01834	0.01919
$\Delta E(ASPE\ \Psi_4)$[d]	0.00583	0.00552	0.00664	0.00696	0.00770	0.00805	0.00785	0.00834
	91.92%	94.15%	94.04%	94.48%	94.51%	94.76%	95.27%	95.33%
$\Delta E(SP)$[e]	0.00594	0.00808	0.01100	0.01280	0.01449	0.01566	0.01623	0.01705
$\Delta E(ASPE)$[f]	0.00440	0.00394	0.00484	0.00511	0.00565	0.00595	0.00574	0.00620
	93.90%	95.82%	95.66%	95.94%	95.97%	96.12%	96.54%	96.53%
E(exact)	-7.50040	-14.66731	-24.34896	-36.53446	-51.22244	-68.41121	-88.09990	-110.28946
			Results of other calculations					
$\Delta E(Watson)$[g]		0.00991						
		89.49%						
$\Delta E(Weiss)$[h]	0.00479	0.00641	0.00764	0.00825	0.00963	0.01112		
	93.36%	93.20%	93.14%	93.45%	93.13%	92.76%		
$\Delta E(Kelly)$[i]		0.00336						
		96.44%						

---

[a] $\Delta E(\cdots) = E(\cdots) - E(exact)$. For every ASPE the per cent correlation energy recovered $100\{[E(HF)-E(ASPE\ \Psi_i)]/\Delta E(HF)\}$ is listed.

[b] E(HF) = Hartree-Fock energy calculated by C. C. J. Roothaan, L. M. Sachs and A. W. Weiss, Rev. Mod. Phys. 32, 186 (1960). Correlation energy = $-\Delta E(HF)$.

[c] $E(APSG\ \Phi_i)$ = energy calculated from antisymmetrized product of separated geminals Φ_i.

[d] $E(ASPE\ \Psi_i)$ = energy calculated from augmented separated pair expansion Ψ_i.

[e] E(SP) = energy of separated pair approximation extrapolated from APSG Φ_4 by including the K-geminal correction.

[f] E(ASPE) = energy of augmented separated pair expansion extrapolated from ASPE Ψ_4 by adding the weighted K-geminal correction $c_0^2\{E(SP)-E(APSG\ \Phi_4)\}$.

[g] E(Watson) = configuration interaction energy calculated by R. E. Watson, Phys. Rev. 119, 170 (1960).

[h] E(Weiss) = energy calculated by A. W. Weiss, Phys. Rev. 122, 1826 (1961).

[i] E(Kelly) = energy calculated by H. P. Kelly, Phys. Rev. 131, 684 (1963), obtained by the application of the Brueckner-Goldstone perturbation theory.

Figure 28. Energies of various augmented separated pair expansions for beryllium-like atoms

Coefficients of augmented separated pair configurations in the augmented separated pair expansion Ψ_2 for beryllium-like atoms

No.	ASPC	Li^-	Be	B^+	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
0	APSG Φ_2	0.99995	0.99992	0.99992	0.99993	0.99994	0.99995	0.99996	0.99996
1	(L2s, L2s; K2p, L2p; 0)	0.00496	0.00720	0.00720	0.00680	0.00640	0.00576	0.00536	0.00480
2	(K2s, K2s; K1s, L2s; 0)	-0.00400	-0.00520	-0.00520	-0.00520	-0.00480	-0.00440	-0.00408	-0.00360
3	(K1s, L2s; K2p, L2p; 1)	-0.00440	-0.00640	-0.00640	-0.00600	-0.00552	-0.00480	-0.00456	-0.00400
6	(K1s, L2s; K2p, K2p; 0)	0.00320	0.00400	0.00400	0.00400	0.00360	0.00336	0.00304	0.00280
8	(K1s, L2s; K2p, L2p; 0)	-0.00200	-0.00200	-0.00160	-0.00120	-0.00080	-0.00040	-0.00040	0.00000
9	(K2s, L2s; L2p, L2p; 0)	-0.00240	-0.00240	-0.00200	-0.00192	-0.00160	-0.00160	-0.00120	-0.00120
10	(K1s, L2s; L2p, L2p; 0)	0.00368	0.00360	0.00280	0.00240	0.00200	0.00160	0.00104	0.00120
12	(K1s, K1s; K2s, K2s; 0)	-0.00056	-0.00120	-0.00160	-0.00200	-0.00200	-0.00192	-0.00184	-0.00200
15	(K1s, K2s; K2p, L2p; 0)	0.00096	0.00120	0.00120	0.00120	0.00112	0.00096	0.00096	0.00080
22	(L2s, L2s; L2p, L2p; 0)	0.00016	0.00080	0.00120	0.00160	0.00160	0.00176	0.00176	0.00160
26	(K1s, K1s; K2p, L2p; 0)	0.00104	0.00120	0.00120	0.00080	0.00080	0.00064	0.00056	0.00080

Figure 29. Coefficients of augmented separated pair configurations in the augmented separated pair expansion Ψ_2 for beryllium-like atoms

Coefficients of augmented separated pair configurations in the augmented separated pair expansion Ψ_3 for beryllium-like atoms

No.	ASPC	Li^-	Be	B^+	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
0	APSG Φ_3	0.99993	0.99988	0.99989	0.99991	0.99993	0.99994	0.99995	0.99995
1	(L2s, L2s; K2p, L2p; 0)	0.00520	0.00760	0.00760	0.00720	0.00672	0.00640	0.00584	0.00520
2	(K2s, K2s; K1s, L2s; 0)	-0.00584	-0.00720	-0.00680	-0.00624	-0.00560	-0.00496	-0.00448	-0.00400
3	(K1s, L2s; K2p, L2p; 1)	-0.00488	-0.00720	-0.00720	-0.00680	-0.00600	-0.00560	-0.00520	-0.00480
5	(K1s, L2s; K2p, K3p; 0)	-0.00128	-0.00176	-0.00176	-0.00144	-0.00120	-0.00104	-0.00104	-0.00080
6	(K1s, L2s; K2p, K2p; 0)	0.00224	0.00280	0.00280	0.00280	0.00280	0.00256	0.00240	0.00240
7	(K1s, L2s; K2p, K3p; 1)	-0.00096	-0.00144	-0.00144	-0.00136	-0.00120	-0.00104	-0.00096	-0.00080
8	(K1s, L2s; K2p, L2p; 0)	-0.00280	-0.00400	-0.00322	-0.00280	-0.00200	-0.00152	-0.00128	-0.00120
9	(K2s, L2s; L2p, L2p; 0)	-0.00312	-0.00280	-0.00240	-0.00200	-0.00160	-0.00144	-0.00136	-0.00120
10	(K1s, L2s; L2p, L2p; 0)	0.00432	0.00400	0.00320	0.00240	0.00200	0.00160	0.00120	0.00120
12	(K1s, K1s; K2s, K2s; 0)	-0.00112	-0.00200	-0.00240	-0.00240	-0.00224	-0.00216	-0.00208	-0.00200
14	(K1s, L2s; L2p, K3p; 0)	-0.00088	-0.00160	-0.00160	-0.00144	-0.00120	-0.00096	-0.00088	-0.00080
15	(K1s, K2s; K2p, L2p; 0)	0.00128	0.00160	0.00160	0.00120	0.00120	0.00104	0.00096	0.00080
16	(K1s, L2s; K3s, K3s; 0)	-0.00048	-0.00056	-0.00056	-0.00064	-0.00064	-0.00064	-0.00056	-0.00040
19	(K1s, L2s; K2s, K3s; 0)	-0.00032	-0.00040	-0.00040	-0.00056	-0.00048	-0.00040	-0.00032	-0.00040
22	(L2s, L2s; L2p, L2p; 0)	0.00008	0.00080	0.00160	0.00160	0.00160	0.00184	0.00160	0.00160
23	(K1s, L2s; K3p, K3p; 0)	0.00048	0.00064	0.00064	0.00064	0.00064	0.00056	0.00048	0.00040
26	(K1s, K1s; K2p, L2p; 0)	0.00120	0.00120	0.00120	0.00080	0.00080	0.00064	0.00066	0.00080
27	(K1s, L2s; K3d, K3d; 0)	-0.00056	-0.00064	-0.00064	-0.00064	-0.00056	-0.00056	-0.00053	-0.00040

Figure 30. Coefficients of augmented separated pair configurations in the augmented separated pair expansion Ψ_3 for beryllium-like atoms

Coefficients of augmented separated pair configurations in the augmented separated pair expansion Ψ_4 for beryllium-like atoms

No.	ASPC	Li$^-$	Be	B$^+$	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
0	APSG Φ_4	0.99974	0.99984	0.99987	0.99989	0.99991	0.99993	0.99994	0.99994
1	(L2s, L2s; K2p, L2p; 0)	0.00520	0.00760	0.00760	0.00728	0.00680	0.00632	0.00576	0.00520
2	(K2s, K2s; K1s, L2s; 0)	-0.00592	-0.00680	-0.00648	-0.00608	-0.00528	-0.00488	-0.00440	-0.00400
3	(K1s, L2s; K2p, L2p; 1)	-0.00496	-0.00680	-0.00720	-0.00680	-0.00600	-0.00560	-0.00520	-0.00440
4	(K1s, L2s; L3p, K2p; 1)	-0.00608	-0.00600	-0.00480	-0.00400	-0.00360	-0.00280	-0.00248	-0.00200
5	(K1s, L2s; K2p, K3p; 0)	-0.00184	-0.00240	-0.00216	-0.00192	-0.00160	-0.00136	-0.00120	-0.00104
6	(K1s, L2s; K2p, K2p; 0)	0.00176	0.00240	0.00280	0.00240	0.00240	0.00248	0.00240	0.00200
7	(K1s, L2s; K2p, K3p; 1)	-0.00184	-0.00256	-0.00264	-0.00240	-0.00208	-0.00184	-0.00168	-0.00160
8	(K1s, L2s; K2p, L2p; 0)	-0.00320	-0.00400	-0.00320	-0.00280	-0.00200	-0.00160	-0.00136	-0.00080
9	(K2s, L2s; L2p, L2p; 0)	-0.00280	-0.00240	-0.00240	-0.00200	-0.00168	-0.00160	-0.00136	-0.00120
10	(K1s, L2s; L2p, L2p; 0)	0.00440	0.00440	0.00320	0.00240	0.00240	0.00160	0.00144	0.00160
11	(K1s, L2s; L3p, K2p; 0)	0.00280	0.00256	0.00200	0.00160	0.00128	0.00112	0.00096	0.00080
12	(K1s, K1s; K2s, K2s; 0)	-0.00104	-0.00200	-0.00240	-0.00248	-0.00240	-0.00232	-0.00208	-0.00216
13	(K1s, L2s; K3d, K4d; 0)	0.00040	0.00080	0.00080	0.00080	0.00080	0.00080	0.00064	0.00080
14	(K1s, L2s; L2p, K3p; 0)	-0.00120	-0.00200	-0.00160	-0.00160	-0.00120	-0.00104	-0.00104	-0.00080
15	(K1s, K2s; K2p, L2p; 0)	0.00128	0.00160	0.00160	0.00128	0.00120	0.00112	0.00096	0.00080
16	(K1s, L2s; K3s, K3s; 0)	-0.00048	-0.00080	-0.00064	-0.00072	-0.00064	-0.00064	-0.00048	-0.00040
17	(K1s, L2s; L3p, K3p; 1)	-0.00192	-0.00200	-0.00160	-0.00128	-0.00112	-0.00088	-0.00080	-0.00064
18	(K1s, L2s; K3p, K4p; 0)	-0.00024	-0.00040	-0.00040	-0.00040	-0.00032	-0.00032	-0.00032	-0.00024
19	(K1s, L2s; K2s, K3s; 0)	-0.00048	-0.00048	-0.00016	-0.00008	0.00000	0.00000	0.00000	0.00000
20	(K1s, L2s; K2p, K4p; 1)	-0.00072	-0.00096	-0.00120	-0.00120	-0.00104	-0.00096	-0.00080	-0.00080
21	(K1s, L2s; K3d, L3d; 1)	-0.00056	-0.00080	-0.00080	-0.00080	-0.00080	-0.00064	-0.00064	-0.00040
22	(L2s, L2s; L2p, L2p; 0)	0.00016	0.00120	0.00160	0.00160	0.00168	0.00168	0.00160	0.00160
23	(K1s, L2s; K3p, K3p; 0)	0.00024	0.00024	0.00040	0.00040	0.00032	0.00032	0.00032	0.00040
24	(K1s, L2s; K3d, K4d; 1)	0.00016	0.00040	0.00040	0.00040	0.00040	0.00032	0.00032	0.00040
25	(K1s, L2s; K3d, L3d; 0)	0.00040	0.00080	0.00080	0.00080	0.00080	0.00080	0.00064	0.00080
26	(K1s, K1s; K2p, L2p; 0)	0.00120	0.00120	0.00160	0.00120	0.00120	0.00080	0.00088	0.00040
27	(K1s, L2s; K3d, K3d; 0)	-0.00032	-0.00024	0.00000	-0.00008	-0.00008	0.00000	-0.00008	0.00000
28	(K1s, L2s; L3d, K4d; 0)	0.00016	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040

Figure 31. Coefficients of augmented separated pair configurations in the augmented separated pair expansion Ψ_4 for beryllium-like atoms

Energy analysis of augmented separated pair expansion Ψ_2 for beryllium-like atoms

No.	Contribution[a]	Li^-	Be	B^+	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
0	E(APSG Φ_2)	-7.48419	-14.64809	-24.32561	-36.50775	-51.19208	-68.37788	-88.06437	-110.25118
1	ΔE(L2s, L2s; K2p, L2p; 0)	-0.00022	-0.00086	-0.00144	-0.00192	-0.00234	-0.00258	-0.00287	-0.00297
2	ΔE(K2s, K2s; K1s, L2s; 0)	-0.00024	-0.00072	-0.00107	-0.00139	-0.00157	-0.00168	-0.00179	-0.00178
3	ΔE(K1s, L2s; K2p, L2p; 1)	-0.00013	-0.00051	-0.00084	-0.00110	-0.00130	-0.00138	-0.00156	-0.00158
6	ΔE(K1s, L2s; K2p, K2p; 0)	-0.00012	-0.00036	-0.00058	-0.00081	-0.00094	-0.00111	-0.00118	-0.00127
8	ΔE(K1s, L2s; K2p, L2p; 0)	-0.00003	-0.00006	-0.00006	-0.00005	-0.00004	-0.00002	-0.00002	0.00000
9	ΔE(K2s, L2s; L2p, L2p; 0)	-0.00005	-0.00010	-0.00012	-0.00015	-0.00015	-0.00017	-0.00015	-0.00016
10	ΔE(K1s, L2s; L2p, L2p; 0)	-0.00003	-0.00006	-0.00006	-0.00006	-0.00006	-0.00005	-0.00003	-0.00004
12	ΔE(K1s, K1s; K2s, K2s; 0)	0.00000	-0.00003	-0.00007	-0.00016	-0.00021	-0.00025	-0.00029	-0.00036
15	ΔE(K1s, K2s; K2p, L2p; 0)	-0.00001	-0.00003	-0.00005	-0.00007	-0.00008	-0.00008	-0.00010	-0.00009
22	ΔE(L2s, L2s; L2p, L2p; 0)	0.00000	-0.00001	-0.00002	-0.00006	-0.00008	-0.00012	-0.00016	-0.00018
26	ΔE(K1s, K1s; K2p, L2p; 0)	-0.00001	-0.00001	-0.00002	-0.00001	-0.00002	-0.00001	-0.00001	-0.00002
	ΔE(ASPC)[b]	-0.00084	-0.00275	-0.00434	-0.00578	-0.00679	-0.00745	-0.00816	-0.00845
	E(ASPE Ψ_2)-E(APSG Φ_2)	-0.00084	-0.00277	-0.00440	-0.00571	-0.00674	-0.00746	-0.00816	-0.00855
	E(ASPE Ψ_2)	-7.48503	-14.65086	-24.33001	-36.51346	-51.19882	-68.38534	-88.07253	-110.25973

[a] The symbol $\Delta E(\mu i, \nu j; \mu' i', \nu' j'; \alpha)$ denotes the contribution $c_0 c_n H_{0n}$ of the indicated ASPC to the energy lowering beyond the separated pair approximation E(APSG Φ_2).

[b] ΔE(ASPC) is the sum over all energy contributions $c_0 c_n H_{0n}$. The slight difference between ΔE(ASPC) and {E(ASPE Ψ_2)-E(APSG Φ_2)} is discussed in the text.

Figure 32. Energy analysis of augmented separated pair expansion Ψ_2 for beryllium-like atoms

Energy analysis of augmented separated pair expansion Ψ_3 for beryllium-like atoms

No.	Contribution[a]	Li^-	Be	B^+	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
0	E(APSG Φ_3)	-7.49126	-14.65515	-24.33329	-36.51660	-51.20223	-68.38950	-88.07757	-110.26611
1	ΔE(L2s, L2s; K2p, L2p; 0)	-0.00022	-0.00090	-0.00149	-0.00200	-0.00242	-0.00283	-0.00306	-0.00317
2	ΔE(K2s, K2s; K1s, L2s; 0)	-0.00030	-0.00087	-0.00124	-0.00150	-0.00168	-0.00180	-0.00187	-0.00195
3	ΔE(K1s, L2s; K2p, L2p; 1)	-0.00015	-0.00059	-0.00096	-0.00126	-0.00143	-0.00162	-0.00178	-0.00189
5	ΔE(K1s, L2s; K2p, K3p; 0)	-0.00007	-0.00023	-0.00034	-0.00038	-0.00039	-0.00040	-0.00047	-0.00041
6	ΔE(K1s, L2s; K2p, K2p; 0)	-0.00007	-0.00021	-0.00034	-0.00048	-0.00063	-0.00070	-0.00078	-0.00093
7	ΔE(K1s, L2s; K2p, K3p; 1)	-0.00002	-0.00010	-0.00015	-0.00019	-0.00021	-0.00021	-0.00023	-0.00021
8	ΔE(K1s, L2s; K2p, L2p; 0)	-0.00004	-0.00013	-0.00014	-0.00013	-0.00010	-0.00007	-0.00006	-0.00005
9	ΔE(K2s, L2s; L2p, L2p; 0)	-0.00007	-0.00012	-0.00014	-0.00014	-0.00014	-0.00015	-0.00016	-0.00016
10	ΔE(K1s, L2s; L2p, L2p; 0)	-0.00004	-0.00007	-0.00007	-0.00006	-0.00006	-0.00005	-0.00004	-0.00004
12	ΔE(K1s, K1s; K2s, K2s; 0)	-0.00001	-0.00006	-0.00012	-0.00018	-0.00023	-0.00027	-0.00031	-0.00035
14	ΔE(K1s, L2s; L2p, K3p; 0)	-0.00001	-0.00004	-0.00007	-0.00009	-0.00010	-0.00010	-0.00011	-0.00011
15	ΔE(K1s, K2s; K2p, L2p; 0)	-0.00002	-0.00005	-0.00007	-0.00007	-0.00008	-0.00009	-0.00009	-0.00009
16	ΔE(K1s, L2s; K3s, K3s; 0)	-0.00001	-0.00004	-0.00006	-0.00008	-0.00011	-0.00012	-0.00012	-0.00009
19	ΔE(K1s, L2s; K2s, K3s; 0)	0.00001	0.00003	0.00005	0.00009	0.00010	0.00010	0.00009	0.00013
22	ΔE(L2s, L2s; L2p, L2p; 0)	0.00000	-0.00002	-0.00003	-0.00005	-0.00008	-0.00012	-0.00014	-0.00017
23	ΔE(K1s, L2s; K3p, K3p; 0)	-0.00002	-0.00005	-0.00007	-0.00010	-0.00014	-0.00014	-0.00014	-0.00013
26	ΔE(K1s, K1s; K2p, L2p; 0)	-0.00001	-0.00001	-0.00002	-0.00001	-0.00002	-0.00001	-0.00001	-0.00001
27	ΔE(K1s, L2s; K3d, K3d; 0)	-0.00001	-0.00002	-0.00004	-0.00005	-0.00005	-0.00006	-0.00006	-0.00005
	ΔE(ASPC)[b]	-0.00106	-0.00348	-0.00530	-0.00668	-0.00777	-0.00864	-0.00934	-0.00968
	E(ASPE Ψ_3)-E(APSG Φ_3)	-0.00106	-0.00342	-0.00535	-0.00683	-0.00797	-0.00872	-0.00945	-0.00976
	E(ASPE Ψ_3)	-7.49232	-14.65857	-24.33864	-36.52343	-51.21020	-68.39822	-88.08702	-110.27587

[a] The symbol $\Delta E(\mu i,\ \nu j;\ \mu' i',\ \nu' j';\ \alpha)$ denotes the contribution $c_0 c_n H_{0n}$ of the indicated ASPC to the energy lowering beyond the separated pair approximation E(APSG Φ_3).

[b] ΔE(ASPC) is the sum over all energy contributions $c_0 c_n H_{0n}$. The slight difference between ΔE(ASPC) and {E(ASPE Ψ_3)-E(APSG Φ_3)} is discussed in the text.

Figure 33. Energy analysis of augmented separated pair expansion Ψ_3 for beryllium-like atoms

Energy analysis of augmented separated pair expansion Ψ_4 for beryllium-like atoms

No.	Contribution[a]	Li$^-$	Be	B$^+$	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
0	E(APSG Φ_4)	-7.49303	-14.65765	-24.33616	-36.51981	-51.20590	-68.39345	-88.08156	-110.27027
1	ΔE(L2s, L2s; K2p, L2p; 0)	-0.00022	-0.00089	-0.00149	-0.00202	-0.00244	-0.00280	-0.00303	-0.00317
2	ΔE(K2s, K2s; K1s, L2s; 0)	-0.00031	-0.00083	-0.00118	-0.00146	-0.00157	-0.00175	-0.00183	-0.00191
3	ΔE(K1s, L2s; K2p, L2p; 1)	-0.00015	-0.00056	-0.00096	-0.00126	-0.00144	-0.00163	-0.00179	-0.00175
4	ΔE(K1s, L2s; L3p, K2p; 1)	-0.00017	-0.00032	-0.00034	-0.00034	-0.00038	-0.00033	-0.00033	-0.00030
5	ΔE(K1s, L2s; K2p, K3p; 0)	-0.00010	-0.00030	-0.00041	-0.00049	-0.00051	-0.00051	-0.00053	-0.00052
6	ΔE(K1s, L2s; K2p, K2p; 0)	-0.00006	-0.00019	-0.00035	-0.00042	-0.00054	-0.00070	-0.00080	-0.00078
7	ΔE(K1s, L2s; K2p, K3p; 1)	-0.00005	-0.00018	-0.00028	-0.00034	-0.00036	-0.00038	-0.00040	-0.00043
8	ΔE(K1s, L2s; K2p, L2p; 0)	-0.00005	-0.00013	-0.00014	-0.00014	-0.00011	-0.00008	-0.00007	-0.00004
9	ΔE(K2s, L2s; L2p, L2p; 0)	-0.00006	-0.00010	-0.00014	-0.00014	-0.00014	-0.00016	-0.00016	-0.00016
10	ΔE(K1s, L2s; L2p, L2p; 0)	-0.00004	-0.00009	-0.00008	-0.00007	-0.00008	-0.00005	-0.00005	-0.00006
11	ΔE(K1s, L2s; L3p, K2p; 0)	-0.00005	-0.00008	-0.00008	-0.00007	-0.00008	-0.00007	-0.00007	-0.00006
12	ΔE)K1s, K1s; K2s, K2s; 0)	-0.00001	-0.00006	-0.00012	-0.00018	-0.00023	-0.00028	-0.00030	-0.00037
13	ΔE(K1s, L2s; K3d, K4d; 0)	-0.00001	-0.00006	-0.00009	-0.00012	-0.00016	-0.00019	-0.00018	-0.00025
14	ΔE(K1s, L2s; L2p, K3p; 0)	-0.00001	-0.00006	-0.00008	-0.00011	-0.00010	-0.00011	-0.00013	-0.00012
15	ΔE(K1s, K2s; K2p, L2p; 0)	-0.00002	-0.00004	-0.00007	-0.00007	-0.00008	-0.00010	-0.00010	-0.00009
16	ΔE(K1s, L2s; K3s, K3s; 0)	-0.00001	-0.00004	-0.00006	-0.00008	-0.00010	-0.00011	-0.00010	-0.00009
17	ΔE(K1s, L2s; L3p, K3p; 1)	-0.00002	-0.00004	-0.00004	-0.00004	-0.00005	-0.00004	-0.00004	-0.00004
18	ΔE(K1s, L2s; K3p, K4p; 0)	-0.00001	-0.00003	-0.00004	-0.00005	-0.00006	-0.00007	-0.00008	-0.00007
19	ΔE(K1s, L2s; K2s, K3s; 0)	0.00002	0.00003	0.00002	0.00001	0.00000	0.00000	0.00000	0.00000
20	ΔE(K1s, L2s; K2p, K4p; 1)	-0.00001	-0.00002	-0.00005	-0.00006	-0.00007	-0.00008	-0.00007	-0.00008
21	ΔE(K1s, L2s; K3d, L3d; 1)	0.00000	-0.00002	-0.00003	-0.00003	-0.00005	-0.00005	-0.00005	-0.00004
22	ΔE(L2s, L2s; L2p, L2p; 0)	0.00000	-0.00001	-0.00003	-0.00006	-0.00009	-0.00012	-0.00014	-0.00018
23	ΔE(K1s, L2s; K3p, K3p; 0)	-0.00001	-0.00001	-0.00004	-0.00006	-0.00006	-0.00007	-0.00008	-0.00012
24	ΔE(K1s, L2s; K3d, K4d; 1)	0.00000	-0.00001	-0.00002	-0.00002	-0.00003	-0.00003	-0.00004	-0.00006
25	ΔE(K1s, L2s; K3d, L3d; 0)	0.00000	-0.00001	-0.00002	-0.00002	-0.00003	-0.00004	-0.00003	-0.00005
26	ΔE(K1s, K1s; K2p, L2p; 0)	-0.00001	-0.00001	-0.00003	-0.00003	-0.00003	-0.00002	-0.00003	-0.00001
27	ΔE(K1s, L2s; K3d, K3d; 0)	0.00000	-0.00001	0.00000	-0.00001	-0.00001	0.00000	-0.00001	0.00000
28	ΔE(K1s, L2s; L3d, K4d; 0)	0.00000	0.00000	-0.00001	-0.00001	-0.00001	-0.00002	-0.00002	-0.00002
	ΔE(ASPC)[b]	-0.00136	-0.00407	-0.00616	-0.00769	-0.00881	-0.00979	-0.01046	-0.01077
	E(ASPE Ψ_4)-E(APSG Φ_4)	-0.00154	-0.00414	-0.00616	-0.00769	-0.00884	-0.00971	-0.01049	-0.01085
	E(ASPE Ψ_4)	-7.49457	-14.66179	-24.34232	-36.52750	-51.21474	-68.40316	-88.09205	-110.28112

[a] The symbol $\Delta E(\mu i, \nu j; \mu' i', \nu' j'; \alpha)$ denotes the contribution $c_0 c_n H_{0n}$ of the indicated ASPC to the energy lowering beyond the separated pair approximation E(APSG Φ_4).

[b] ΔE(ASPC) is the sum over all energy contributions $c_0 c_n H_{0n}$. The slight difference between ΔE(ASPC) and {E(ASPE Ψ_4)-E(APSG Φ_4)} is discussed in the text.

Figure 34. Energy analysis of augmented separated pair expansion Ψ_4 for beryllium-like atoms

Comparative analysis of energy lowering of ASPE's and comparison with perturbation theory

Energy[a]	Number of ASPC's	Li^-	Be	B^+	C^{+2}	N^{+3}	O^{+4}	F^{+5}	Ne^{+6}
				Augmented separated pair expansion Ψ_2					
$\Delta\epsilon_2$	11	-0.00084	-0.00275	-0.00434	-0.00578	-0.00679	-0.00745	-0.00816	-0.00845
$\Delta\epsilon_T(P)$		-0.00085	-0.00279	-0.00443	-0.00570	-0.00670	-0.00744	-0.00814	-0.00862
				Augmented separated pair expansion Ψ_3					
$\Delta\epsilon_2$	11	-0.00093	-0.00303	-0.00462	-0.00588	-0.00687	-0.00771	-0.00830	-0.00881
$\Delta\epsilon_3$	7	-0.00013	-0.00045	-0.00068	-0.00080	-0.00090	-0.00093	-0.00104	-0.00087
$\Delta\epsilon_T$	18	-0.00106	-0.00348	-0.00530	-0.00668	-0.00777	-0.00864	-0.00934	-0.00968
$\Delta\epsilon_T(P)$		-0.00115	-0.00371	-0.00579	-0.00738	-0.00854	-0.00952	-0.01031	-0.01076
				Augmented separated pair expansion Ψ_4					
$\Delta\epsilon_2$	11	-0.00093	-0.00291	-0.00459	-0.00585	-0.00675	-0.00769	-0.00830	-0.00852
$\Delta\epsilon_3$	7	-0.00016	-0.00057	-0.00085	-0.00108	-0.00114	-0.00118	-0.00125	-0.00128
$\Delta\epsilon_4$	10	-0.00027	-0.00059	-0.00072	-0.00076	-0.00092	-0.00092	-0.00091	-0.00097
$\Delta\epsilon_T$	28	-0.00136	-0.00407	-0.00616	-0.00769	-0.00881	-0.00979	-0.01046	-0.01077
$\Delta\epsilon_T(P)$		-0.00149	-0.00437	-0.00646	-0.00847	-0.00984	-0.01043	-0.01178	-0.01253

---

[a] $\Delta\epsilon_i$ denotes the contribution to the energy lowering beyond the separated pair approximation resulting from those ASPC's which occur in Ψ_i but not in Ψ_{i-1}. $\Delta\epsilon_T = \Sigma\Delta\epsilon_i$ is the total energy lowering beyond the separated pair approximation. $\Delta\epsilon_T(P)$ is the total energy lowering calculated from second order perturbation theory.

Figure 35. Comparative analysis of energy lowering of ASPE's and comparison with perturbation theory

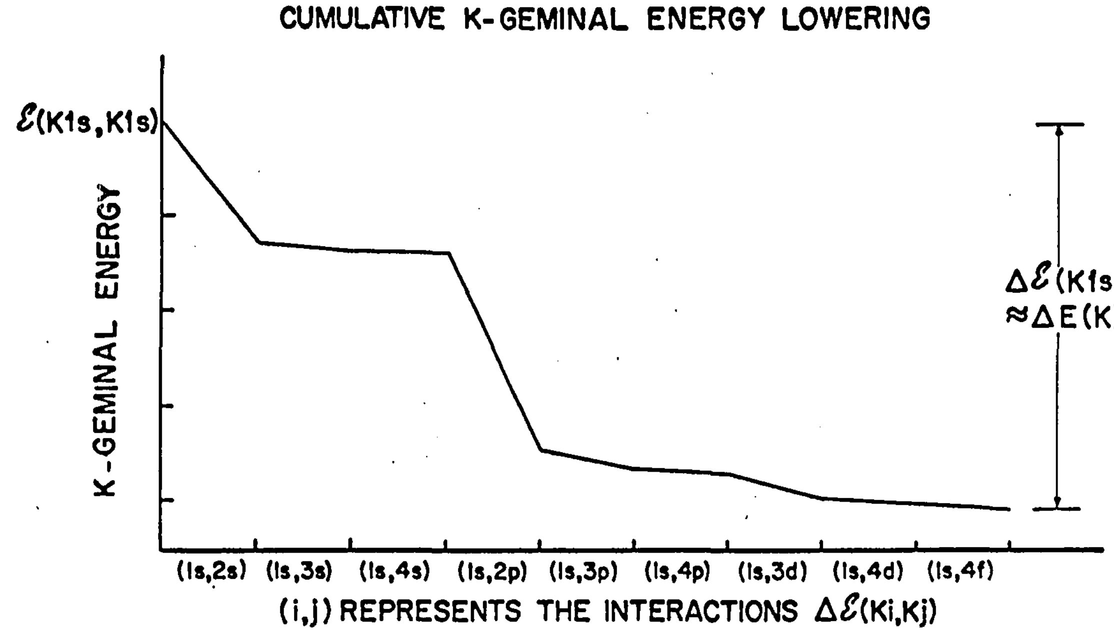
Comparison between variational calculation and perturbation calculation for beryllium for augmented separated pair expansion Ψ_3

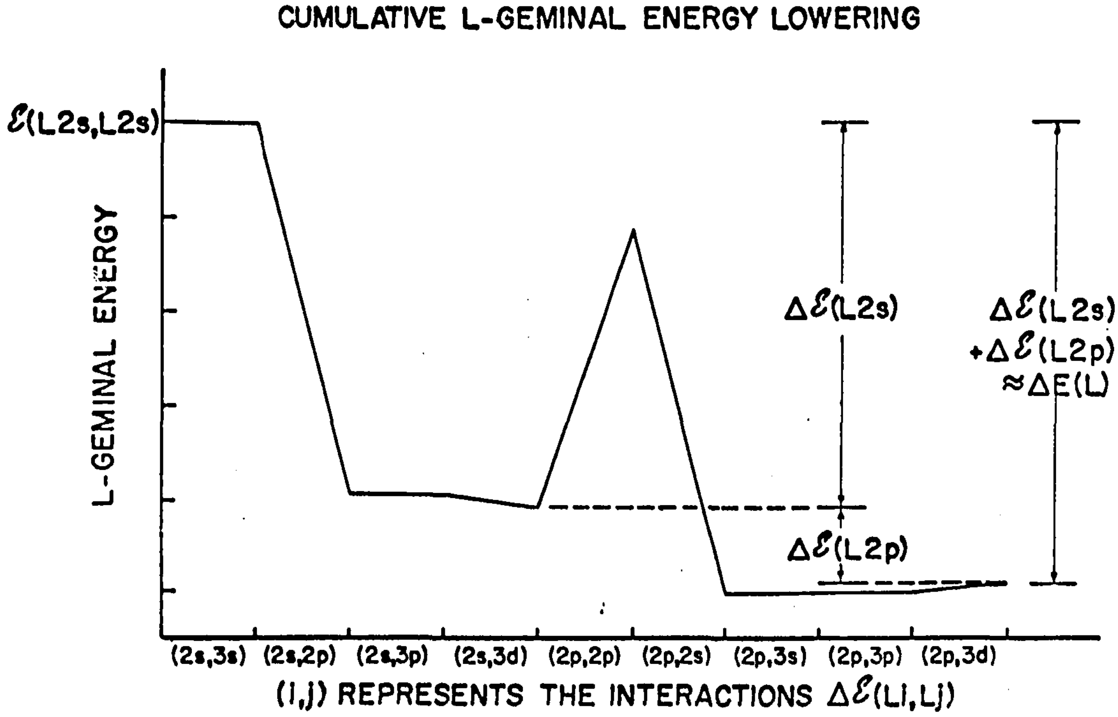
No. (n)	$\frac{H_{0n}}{H_{00}-H_{nn}}$	δc_n [a]	$\frac{H_{0n}H_{n0}}{H_{00}-H_{nn}}$	$\delta(\Delta E_n)$ [b]
1	0.00756	0.00004	-0.00089	-0.00001
2	-0.00686	-0.00034	-0.00082	-0.00005
3	-0.00723	0.00003	-0.00059	0.00000
5	-0.00276	0.00100	-0.00035	0.00012
6	0.00406	-0.00126	-0.00031	0.00010
7	-0.00146	0.00002	-0.00010	0.00000
8	-0.00295	-0.00105	-0.00009	-0.00004
9	-0.00268	-0.00012	-0.00011	-0.00001
10	0.00392	0.00008	-0.00007	0.00000
12	-0.00185	-0.00015	-0.00005	-0.00001
14	-0.00069	-0.00091	-0.00002	-0.00002
15	0.00153	0.00007	-0.00005	0.00000
16	-0.00058	0.00002	-0.00004	0.00000
19	0.00113	-0.00153	-0.00009	0.00012
22	0.00074	0.00006	-0.00001	0.00000
23	0.00103	-0.00039	-0.00008	0.00003
26	0.00131	-0.00011	-0.00001	0.00000
27	-0.00079	0.00015	-0.00003	0.00000
Total			-0.00371	0.00023

[a] This error is defined by $c_n = H_{0n}/[H_{00}-H_{nn}] + \delta c_n$ where c_n is the coefficient of the n-th ASPC in ASPE Ψ_3.

[b] This error is defined by $\Delta E_n = H_{0n}^2/[H_{00}-H_{nn}] + \delta(\Delta E_n)$ where ΔE_n is the energy lowering contribution $c_0 c_n H_{0n}$ of the n-th ASPC in ASPE Ψ_3.

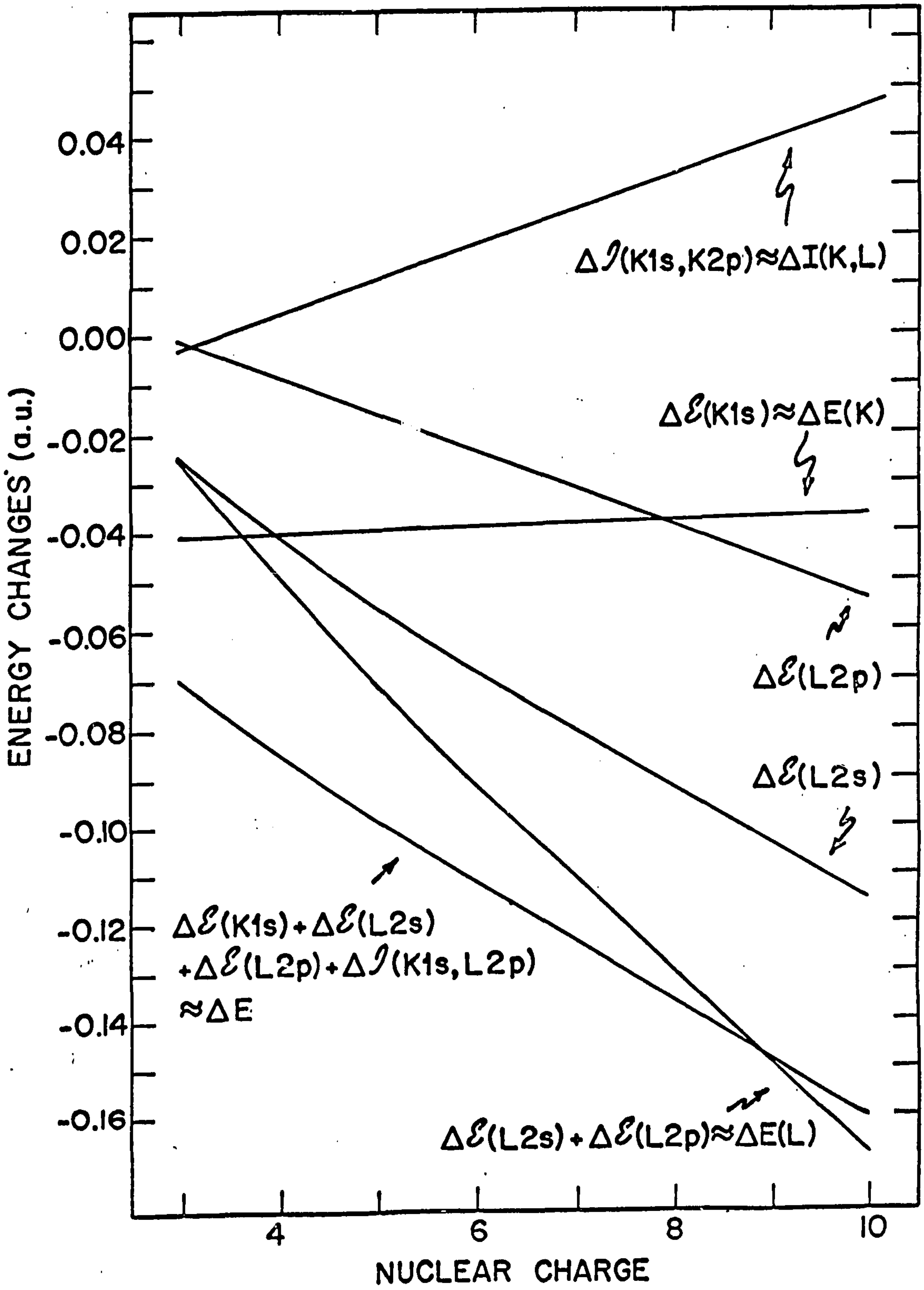
Figure 36. Comparison between variational calculation and perturbation calculation for beryllium for augmented separated pair expansion Ψ_3

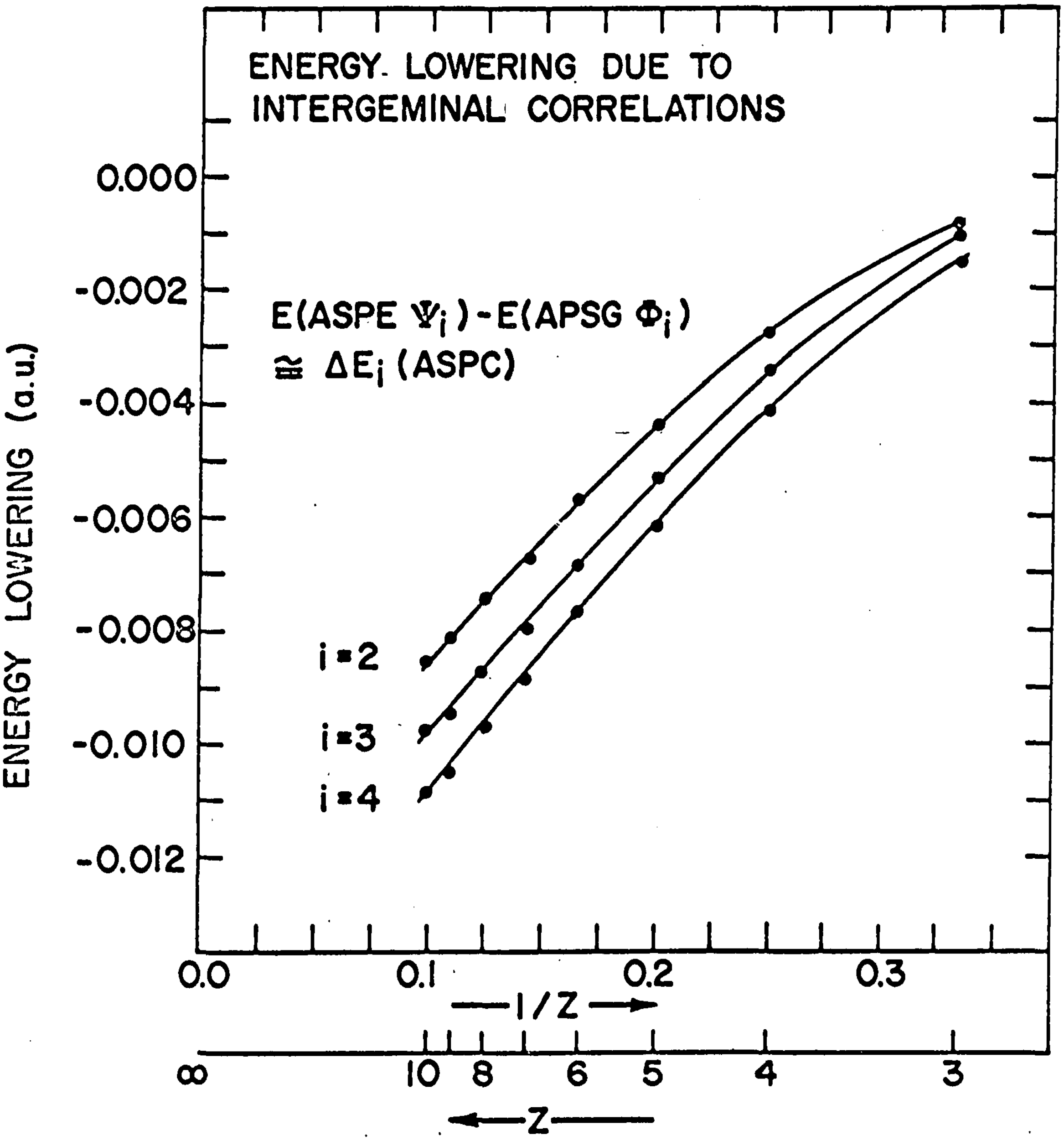




Graph 1. Analysis of intrageminal contributions to energy lowering in the separated pair approximation

Graph 2. Dependence upon nuclear charge of intrageminal and intergeminal contributions to energy lowering in the separated pair approximation


ENERGY CHANGES (a.u.)
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14
-0.16
NUCLEAR CHARGE
4
6
8
10
$\Delta\mathcal{J}$(K1s,K2p)≈ΔI(K,L)
$\Delta\mathcal{E}$(K1s)≈ΔE(K)
$\Delta\mathcal{E}$(L2p)
$\Delta\mathcal{E}$(L2s)
$\Delta\mathcal{E}$(K1s)+$\Delta\mathcal{E}$(L2s) +$\Delta\mathcal{E}$(L2p)+$\Delta\mathcal{J}$(K1s,L2p) ≈ΔE
$\Delta\mathcal{E}$(L2s)+$\Delta\mathcal{E}$(L2p)≈ΔE(L)



Graph 3. Energy lowering due to intergeminal correlations for the augmented separated pair expansion