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Studies of the correlation energy

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City University of New York, 1990

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STUDIES OF THE CORRELATION ENERGY

BY

XUE-QIN GAO

A dissertation submitted to the graduate faculty in chemistry in partial fulfillment of the requirements for the degree of doctor of philosophy, The City of University of New York.

1990

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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ABSTRACT

STUDIES OF THE CORRELATION ENERGY

BY

XUE-QIN GAO

ADVISOR: PROFESSOR LOU MASSA

Colle and Salvetti introduced a method to calculate the correlation energy Ec, based upon a correlated wavefunction which is obtained by multiplying a single determinant by a correlation factor.

In this thesis the Colle and Salvetti theoretical and numerical formulas are tested with He, Be, Ne and their isoelectronic series up to z=36. We find the Colle-Salvetti formulas break down for ions with high value of Z.

We investigate a new formalism for calculating the correlation energy Ec. It is inspired by Colle and Salvetti's work, but differs in emphasizing the N-representability of the density matrix. The correlation factor is studied in a generalized form. This new formalism is tested with He and its isoelectronic ions. The calculations of Ec integrals employ our 3 dimensional Simpson integration program without any approximate series expansion. 70% Of the exact correlation energies have been obtained using all terms of the usual Hamiltonian.

Further work to extend our method is suggested.

Acknowledgement

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CONTENTS

APPENDIX

LIST OF TABLES

LIST OF FIGURES

CHAPTER I INTRODUCTION

A definition of correlation energy Ec given by Löwdin [1] is

$$Ec = E_{exact} - E_{HF} \tag{1-1}$$

where HF means the Hartree-Fock value. The electron correlation error of the HF approximation has been recognized as a central problem in atomic structure theory. There are two basic methods for calculating the correlation energy: one involves CI (configuration interaction), another involves correlation factors including interparticle distance vectors.

Colle and Salvetti introduced a method [2] to calculate the correlation energy Ec of a closed-shell system with a correlation factor starting from the known HF orbitals. A number of their results are reported to be close to exact values.

In this dissertation the Colle and Salvetti formalism (C-S formalism) is analyzed using our 3 dimensional Simpson integration program (3D SI). The C-S numerical and theoretical formulas (discussed in chapter III) are used to calculate the correlation energies of He, Be, Ne and their isoelectronic series up to Z=36. In most cases for high values of Z the results from the C-S formalism are not in agreement with nearly exact values from Clementi [3,4], and some results are much lower than the nearly exact value, so that the

Variational principle is violated.

In this thesis the following aspects of the C-S formalism were studied:

<1> The normalization of the density matrix.

<2> Contributions of the correlation energy from kinetic and potential terms in the usual Hamiltonian.

<3> Empirical constants fixed in the C-S fitting procedure.

<4> Results from their theoretical formula and their numerical formula.

In this thesis a quantum chemistry formalism is introduced to improve the C-S procedure.

<1> A parameter t is introduced into the correlation functional to satisfy the normalization of the wave function. The available t value is obtained automatically by our optimizing procedure program.

<2> Kinetic correlation energy Tc and potential correlation energy Vc(2) from the electron-nuclear attraction term were included to improve Ec.

<3> Two variational parameters u and q are used to obtain the optimum Ec, which satisfies the Variational principle.

<4> Highly accurate approximately N-representable density matrices are constructed from a single determinant wave function of the HF orbitals for the calculations [5].

<5> All integrations are carried out using a new 3 dimensional Simpson integration program without any empirical constants and without any fitting procedure. This method

avoids the difficulties arising from a Taylor expansion of the density matrix.

This new formalism is tested with the He atom and its isoelectronic ions. The results supported our formalism as indicated by:

<1> The Calculated Ec has reached 70% and more of the exact correlation energy for the He atom and its isoelectronic series.

<2> Variational parameters for calculating the optimum value of Ec for the He isoelectronic series have been determined.

<3> The relative contribution of all terms contributing to the correlation energy Ec, have been determined. Each term has a clear physical meaning and a reasonable magnitude.

Future work in this area could improve Ec by varying q in smaller intervals. More example calculations of Ec could include the Be and Ne atoms and their isoelectronic series.

CHAPTER II BACKGROUND

(A). The correlation concepts.

If two electrons are non-interactive, from the multiplicative law for the simultaneous occurrence of independent events we have

$$P_2(12) = p_1(1)p_1(2) \qquad (2\text{-}1)$$

where $p_1(1)$ is the diagonal element of the one-body density matrix, and has the meaning of the probability density of finding one electron at point r_1 ; $p_1(2)$ is the diagonal element of the one body density matrix for another electron, with a similar physical meaning; $P_2(12)$ has the meaning of the probability density of finding one electron at point r_1 and another electron at point r_2 simultaneously.

In an interactive situation involving two electrons, a correlation factor is introduced so that

$$P_2(12) = p_1(1)p_1(2)(1+f(12)) \qquad (2\text{-}2)$$

(2-2) could be written as

$$\frac{P_2(12)}{p_1(2)} = p_1(1)(1+ f(12)) \qquad (2\text{-}3)$$

According to probability theory the left side of (2-3) is the conditional probability of finding an electron at point r_1 when another electron is at point r_2.

For point r_1 approaching point r_2 the correlation factor "f" is negative. There is a correlation "hole" in the one-particle probability surrounding any point at which there is already a particle. McWeeny described the correlation hole by a function [6,7]

$$[\ F(1)\ ]_{r_2} = p_1(1)f(12) \qquad (2\text{-}4)$$

Usually the density matrices are defined in terms of wave functions $\Psi(1,\ldots N)$, which depend on both space and spin coordinates. Under the antisymmetric requirement the wave function Ψ may be a single determinant of the orbital $\Phi_m(i)$ with the form

$$\Psi(1,\ldots,N) = \frac{1}{N!} \begin{vmatrix} \Phi_1(1)\ldots. & \Phi_1(N) \\ \vdots & \vdots \\ \Phi_N(1)\ldots. & \Phi_N(N) \end{vmatrix} \qquad (2\text{-}5)$$

$$\Phi_m = \Sigma\ C_k \Omega_k \qquad (2\text{-}6)$$

where Ω_k is an atomic basis, and

$$<\Phi_m \mid \Phi_n> = \delta_{mn} \qquad (2\text{-}7)$$

The Fock-Dirac density matrix [8] is

$$\hat{p}_1(11') = \sum_{i=1}^{N} \phi\ (1)\cdot\phi^*(1') \qquad \text{(A)(2-8)}$$

$$\hat{p}_1(12') = \sum_{i=1}^{N} \phi\ (1)\cdot\phi^*(2') \qquad \text{(B)(2-8)}$$

where $\hat{p}(11')$ and $\hat{p}(12')$ are with spin.

The spinless density matrices which are sometimes desirable, may be obtained by integrating over the spins. For antisymmetric wave functions $\Psi(1,\ldots N)$, the spinless density matrices $p_1(11')$ assume the form

$$p_1(11') = p_1^{\alpha\alpha}(11') + p_1^{\beta\beta}(11') \qquad (2\text{-}9)$$

where $p_1^{\alpha\alpha}(11')$ consists of all the terms in the Fock-Dirac density matrix with spin α, and $p_1^{\beta\beta}(11')$ is the corresponding quantity for spin β. For diagonal elements

$$p_1(1) = p_1^{\alpha}(1) + p_1^{\beta}(1) \qquad (2\text{-}10)$$

where $p_1^{\alpha}(1) = p_1^{\alpha\alpha}(11)$ and $p_1^{\alpha}(1)\cdot d\vec{r}_1$ is the probability of finding an electron with α-spin in the volume element dr_1; $p_1^{\beta}(1) = p_1^{\beta\beta}(11)$ and $p_1^{\beta}(1)\cdot d\vec{r}_1$ has similar meaning.

The diagonal elements of the spinless two-particle density matrix are obtained as

$$P_2(12) = P_2^{\alpha\alpha}(12) + P_2^{\alpha\beta}(12) + P_2^{\beta\alpha}(12) + P_2^{\beta\beta}(12) \tag*{(2-11)}$$

where

$$P_2^{\alpha\alpha}(12) = p_1^{\alpha}(1)p_1^{\alpha}(2) - p_1^{\alpha\alpha}(12)p_1^{\alpha\alpha}(21) \tag*{(A)(2-12)}$$

$$P_2^{\beta\beta}(12) = p_1^{\beta}(1)p_1^{\beta}(2) - p_1^{\beta\beta}(12)p_1^{\beta\beta}(12) \tag*{(B)(2-12)}$$

$$P_2^{\alpha\beta}(12) = p_1^{\alpha}(1)p_1^{\beta}(2) \tag*{(C)(2-12)}$$

$$P_2^{\beta\alpha}(12) = p_1^{\beta}(1)p_1^{\alpha}(2) \tag*{(D)(2-12)}$$

$P_2^{\alpha\alpha}(12)$ is the probability density for finding an electron with α-spin at r_1 and another electron with α-spin at r_2 ; $P_2^{\alpha\beta}(12)$ is the probability density for an electron with α-spin at r_1 and another with β-spin at r_2 , and so forth. The sum $P_2(12)$ is the probability density for an electron at r_1 and another at r_2 irrespective of their spins.

When $r_1 = r_2$, both $P_2^{\alpha\alpha}(12)$ and $P_2^{\beta\beta}(12)$ vanish, $P_2^{\alpha\beta}(12)$ and $P_2^{\beta\alpha}(21)$ do not. This is meaningful according to the Pauli principle which prohibits two electrons with parallel spin from occupying the same point in space but does not impose any restrictions on two electrons with opposite spin.

From formula (2-2), when a correlation factor is brought in, we have

$$P_2^{\alpha\alpha}(12) = p_1^{\alpha}(1)p_1^{\alpha}(2)(1+f^{\alpha\alpha}(12)) \qquad (A)(2\text{-}13)$$

$$P_2^{\alpha\beta}(12) = p_1^{\alpha}(1)p_1^{\beta}(2)(1+f^{\alpha\beta}(1,2)) \qquad (B)(2\text{-}13)$$

From the antisymmetry of the wave function,

$$P_2^{\alpha\alpha}(12) \Big|_{r_1 \to r_2} = 0 \qquad (A)(2\text{-}14)$$

$$P_2^{\beta\beta}(12) \Big|_{r_1 \to r_2} = 0 \qquad (B)(2\text{-}14)$$

This means $f^{\alpha\alpha}(1,2)$ and $f^{\beta\beta}(1,2)$ tend to -1 when r_1r_2. That means, there is zero probability of finding any two electrons with the same spin at the same spatial point, just as the Pauli Principle requires. Correlation arising from the antisymmetry of the electronic wavefunction is usually called the "Fermi correlation".

This restriction does not act on $P_2^{\alpha\beta}(12)$ and $P_2^{\beta\alpha}(12)$, but the electrostatic repulsion still keep electrons with opposite spins apart on the average. This effect is called "Coulomb correlation".

Equation (2-12) show that this single determinant wavefunction only provides correlation for the same spin

$P_2^{\alpha\alpha}(1,2)$ and $P_2^{\beta\beta}(12)$, but for electrons of opposite spin the correlation is absent. In other words, there is only Fermi correlation here, but it fails to describe Coulomb correlation.

(B).The methods with correlation factors including interparticle distance vectors.

This kind of method has been greatly developed since the work of Hylleraas [9,10]. The interelectronic variables were introduced into a two particle wave function and have given solutions with high accuracy in many cases [11-15].

Boys [16] proposed a correlated wave function with a correlation factor as

$$\Psi = C \, \Psi_0 \tag{2-15}$$

where Ψ_0 may be a single Slater determinant, the factor C is a symmetric function containing the interelectronic variables

$$C = \prod_{i<j} F(i,j) \tag{2-16}$$

Boys and Handy [17,18] suggested a modified variational procedure

$$<\delta \, \Psi^+ | \; (H-E) \; | \; \Psi > = 0 \tag{2-17}$$

where

$$\Psi^{+} = C^{-1}\Psi_0 \qquad (2\text{-}18)$$

The equation (2-17) vanishes only when $H\,\Psi = E\,\Psi$, and it is not sensitive to the specific correlation factor used in an arbitrary variation. The functional

$$< \Psi_0 |\ C^{-1}H\ C\ |\ \Psi_0 > \qquad (2\text{-}19)$$

can be regarded as the expectation value of a "transcorrelated Hamiltonian", and is easier to handle than $<\Psi\ |H|\ \Psi>$.

Under suitable forms of F(i,j), very accurate wave functions and highly accurate values of energy have been obtained for the Ne atom [19] and the LiH molecule [20]. Many difficulties may arise when the method is applied to larger systems [7]. The method of Colle and Salvetti, discussed in Chapter 3, is inspired by wavefunctions of the type discussed above.

(C).The CI methods

CI methods have also been highly developed [21,22]. In quantum theory, to expand an N-electron antisymmetric wave function, one needs a complete set of Slater determinants containing N spin orbitals, which are selected from a complete set. The N-electron antisymmetrizer "A" is defined as [23]

$$A = \frac{1}{N!} \sum_{P} (-1)^{P} \hat{P} \qquad (2\text{-}20)$$

From the antisymmetry of the N-body wave function Ψ , we have

$$\Psi = A \Psi \qquad (2\text{-}21)$$

An infinite CI expansion is obtained as

$$\Psi(1,\ldots,N) = \sum_{K}^{M} C_K \Phi_K \qquad (2\text{-}22)$$

where $M \rightarrow \infty$, K represents $k_1, k_2, \ldots k_N$, $k_1 < k_2 \ldots < k_N$, and

$$C_K = (N!)^{\frac{1}{2}} c_{k_1 \ldots k_N} \qquad (2\text{-}23)$$

$$\Phi_K = (N!)^{-\frac{1}{2}} \det(\sigma_{k_1}(1) \ \ldots \ \sigma_{k_N}(N)) \qquad (2\text{-}24)$$

Each of the above Slater determinants correspond to a single electron configuration. Φ_K may represent an orthonormal set of occupied orbitals or an orthonormal set of unoccupied orbitals. Most common methods of CI include the ground state and all single and double excitations to get a limited CI expansion [24].

The most important procedure in CI obtains the coefficients C_K by minimizing the energy with the variational method. This leads to a system of linear equations

$$\sum_j (h_{ij} - E\,\delta_{ij})\,C_K = 0 \qquad (2\text{-}25)$$

where

$$h_{ij} = \langle \Phi_i^* |\, \hat{H} \,| \Phi_j \rangle \qquad (2\text{-}26)$$

The secular determinant is

$$| h_{ij} - E\,\delta_{ij} | = 0 \qquad (2\text{-}27)$$

The C_K are obtained by solving these equations. Although conceptually the CI method should give an arbitrarily accurate N-electron wave function, the convergence is usually slow and the terms which are neglected, may be important.

(D). Correlated determinants from X-ray diffraction.

A correlated single determinant wave function, whose reference state is the single determinant of X-ray orbitals which delivers the exact density, includes correlation effects. Density matrices for many-electron systems which are N-representable by such wave functions are highly accurate.

The Hohenberg and Kohn (HK) theorem [25] states that the many-particle ground state is a unique functional of the electronic density, this means that the electron density contains all the information necessary to evaluate every electronic property of the system. Fortunately,the single crystal coherent X-ray diffraction experiment gives an image of the electron density of crystalline solids. A method has been developed, that constructs the quantum mechanically valid density matrices from the data of the single crystal coherent X-ray diffraction experiment, and then calculates properties of the electrons of the system with these density matrices, which are constructed by single determinant wave functions [26-33]. Remarkably good results for properties of some test systems have been obtained by the calculations with a single determinant of X-ray orbitals [34-37].

When a beam of X-rays shine on a crystal, the radiation is coherently scattered by the electrons in the atoms of the crystal [38], we have

$$F(\vec{k}) = \int e^{i\vec{k}\vec{r}} p(\vec{r})\, d\vec{r} \qquad (2\text{-}28)$$

where $\vec{k}$ is the wave vector, $F(\vec{k})$ is the wave amplitude scattered by the electron distribution $p(\vec{r})$ relative to the scattering by a single electron. This relationship is expressed by a Fourier transformation [39]. The square of the amplitude is proportional to the intensity of the scattered wave from the measurement of the experiment. Certainly the experimentally measured intensity has to be corrected for other effects [40], such as X-ray absorption by the crystal, temperature effect associated with the vibration and so on.

Quantum Mechanics requires that only the densities which are obtainable from the square of an antisymmetric wave functions may be appropriate. The antisymmetric N-body wave function Ψ of (2-5) [41-43] gives an one body reduced density matrix $p_1(11')$ according to the rule

$$p_1(11') = N \int \Psi \ (1,...,N) \ \Psi \ (1',...,N) \ d2...dN \tag{2-29}$$

where the integration is over all the spatial and spin coordinates except the coordinates of one particle. The diagonal element of the first-order density matrix represents the electron density

$$p_1(11') \Big|_{1' \to 1} = p(1) \tag{2-30}$$

For a single determinant (2-5) of orthonormal orbitals, the first order density matrix may be written in a convenient matrix notation as

$$p_1(\vec{r},\vec{r}\,') = \mathrm{tr} \ \underset{\sim}{\Phi}(\vec{r}) \ \underset{\sim}{\Phi}^{+}(\vec{r}\,') \tag{2-31}$$

$$\underset{\sim}{\Phi}(\vec{r}) = \underset{\sim}{C} \ \underset{\sim}{\Omega}(\vec{r}) \tag{2-32}$$

where $\underline{C}$ is a rectangular matrix. From (2-31) we have

$$p_1(\vec{r},\vec{r}\,') = \mathrm{tr}\ \underline{C}^{+}\underline{C}\ \underline{\Omega}(\vec{r})\ \underline{\Omega}(\vec{r}\,') \qquad (2\text{-}33)$$

where $\underline{C}^{+}\underline{C}$ is defined as the population $\underline{P}$

$$\underline{P} = \underline{C}^{+}\underline{C} \qquad (2\text{-}34)$$

The above formulas could be rewritten with the population matrix $\underline{P}$

$$p_1(\vec{r},\vec{r}\,') = \mathrm{tr}\ \underline{P}\ \underline{\Omega}(\vec{r})\ \underline{\Omega}^{+}(\vec{r}\,') \qquad (2\text{-}35)$$

$$p_1(\vec{r}) = \mathrm{tr}\ \underline{P}\ \underline{\Omega}(\vec{r})\ \underline{\Omega}\ (\vec{r}) \qquad (2\text{-}36)$$

$$F(\vec{k}) = \mathrm{tr}\ \underline{P}\ \underline{f}(\vec{k}) \qquad (2\text{-}37)$$

$$\underline{f}_{mn}(\vec{k}) = \int e^{i\ \vec{k}\ \vec{r}}\Omega_m(\vec{r})\ \Omega_n^{*}(\vec{r})\ d\vec{r} \qquad (2\text{-}38)$$

$\underline{P}$ in the equation (2-35) can treat as parameter to be fit to the experimental structure factors. Certainly any fitting procedure should include appropriate Quantum Mechanical restrictions.

For N-representability of the one-body density matrix one has

$$\int p_1(r,r')\ \Phi_i(r')\ dr' = \acute{E}_i\Phi_i \qquad (2\text{-}39)$$

where eigenvalue $\acute{E}_i$ is a number between zero to one, $0 \le \acute{E}_i \le 1$. The physical interpretation of $\acute{E}_i$ is the occupation number of a molecular orbital. In particular,the Ei values 0 and 1 are necessary and sufficient for pl(r,r') to be N-representable by a single determinant of orbitals of the type of equation (2-32) [44].

Furthermore, Gilbert's theorem [45] states that any non-negative density which is normalized to the number of electrons N, is N-representable by a single-determinant wavefunction. Harriman [46] has given a procedure to construct such a determinant from the density, which has single determinant N-representability for $p_1(\vec{r},\vec{r}\,')$.

In the single determinant case [47] one has that

$$\int p_1(\vec{r}\,',\vec{r}\,'')\ p_1(\vec{r}\,'',\vec{r})\ d\vec{r}\,'' = p_1(\vec{r}\,',\vec{r}) \qquad (2\text{-}40)$$

The hermiticity and the normalization are respectively

$$p_1(\vec{r}\,',\vec{r}) = p_1^*(\vec{r},\vec{r}\,') \qquad (2\text{-}41)$$

$$\int P_1(\vec{r},\vec{r})\ d\vec{r} = N \qquad (2\text{-}42)$$

For these conditions to be satisfied by a single determinant of orthonormal orbitals, the population matrix $\underset{\sim}{p}$ is a symmetric normalized projector, and satisfies the experimental structure factors, that is

$$\underset{\sim}{P} = \underset{\sim}{P}^{+} \qquad (A)(2\text{-}43)$$

$$\text{tr}\ \underset{\sim}{P} = N \qquad (B)(2\text{-}43)$$

$$\underset{\sim}{P}^{2} = \underset{\sim}{P} \qquad (C)(2\text{-}43)$$

$$\text{tr}\ \underset{\sim}{P}\ \underset{\sim}{f}(\vec{k}) = F(\vec{k}) \qquad (D)(2\text{-}43)$$

The $\underset{\sim}{p}$ matrix if it is a solution of Clinton's equations (2-44) [48], will satisfy the conditions (2-43)

$$\underset{\sim}{P}_{n+1} = 3\ \underset{\sim}{P}_n^2 - 2\ \underset{\sim}{P}_n^3 + \lambda_K\ \underset{\sim}{f}(k) + \lambda_N\ \underset{\sim}{1} \qquad (2\text{-}44)$$

where λ_K and λ_N are Lagrangian multipliers determined by constraints satisfying structure factors and normalization.

Frishberg and Massa have used the structure factors of Stewart, Davidson and Simpson [49] for the spherical hydrogen atom in a hydrogen molecule as constraints in the determination of the idompotent $\underset{\sim}{P}$ matrix. They showed

Clinton's equations are solvable and yield physically meaningful orbitals.

Frishberg and Massa also investigated the application of the X-ray orbital formalism to bonding effects of H_2 [35]. Their results reproduced the known charge distribution and bond distance of H_2. The structure factors of Li and Be were calculated with X-ray orbitals and HF orbitals in the same basis. In a fit to the exact structure factors, X-ray orbitals gave good quantum properties. HF and X-ray wavefunctions in the same basis were used to calculate a number of properties of Li and Be atoms. The X-ray case gave excellent results (Table 1-1) [34].

One may conclude a single determinant of X-ray orbitals will provide an excellent reference state for correlated determinant wave functions to be used in calculation of correlation energy.

TABLE 2-1 A COMPARISON OF EXACT, HF AND X-RAY ORBITALS SINGLE-DETERMINANT ON SAME BASIS BY SOME EXPECTATION VALUES OF Li AND Be ATOMS [34]

ATOM	$\langle \frac{1}{r} \rangle$	$\langle r^2 \rangle$	$\langle \frac{1}{r_{12}} \rangle$	Kinetic energy	Total energy
Li					
Exact	5.71822	18.35034	2.199	7.478	-7.478025
HF	5.71549	18.62610	2.281	7.433	-7.432749
X-ray	5.71866	18.34609	2.285	7.438	-7.432694
Be					
Exact	8.4246		4.3803	14.66	-14.66090
HF	8.4088	17.32008	4.4891	14.57	-14.57302
X-ray	8.4255	16.32010	4.5376	14.59	-14.57150

CHAPTER III COLLE-SALVETTI FORMALISM FOR THE CORRELATION ENERGY

(A). THE COLLE-SALVETTI FORMULA (C-S Formula)

Colle and Salvetti gave a formalism for approximate calculation of the correlation energy Ec of a closed-shell system, by starting from knowledge of the Hartree-Fock determinant [50-55].

They introduced an approximate N-body wavefunction

$$\Psi(1,\ldots,N) = \Psi^{HF}(1,\ldots,N)\cdot C(r_1,r_2,\ldots,r_N) \tag{3-1}$$

where $\Psi^{HF}(1,2,\ldots,N)$ is the known HF wave function with spin, C is the correlation factor which is spinless, and is taken to be of the form [50]

$$C = \prod_{i<j} [\ 1- \phi(i,j)\ ] \tag{3-2}$$

where $\phi(i,j)$ is a symmetric two-body function which is spinless, and brings in the correlation effects. Colle and Salvetti gave $\phi(i,j)$ a specific form, viz

$$\phi(i,j) = e^{-\beta^2 r^2} (\ 1 - \epsilon(R)\ (\ 1+ \frac{r}{2}\ )) \tag{3-3}$$

where $\epsilon(R)$ is an unknown functional to be determined and

$$r = |\vec{r}_i - \vec{r}_j| \qquad R = \frac{1}{2} |\vec{r}_i + \vec{r}_j| \qquad (3\text{-}4)$$

Equation (3-3) satisfies the appropriate cusp conditions when $\vec{r}_i - \vec{r}_j = 0$ as has been demonstrated by Bingle [56]. When the electrons are far apart, the function Ψ is reduced to that of HF; when a pair of electrons collide, the function becomes

$$\Psi = \Psi^{HF} \epsilon\left(\frac{\vec{r}_i + \vec{r}_j}{2}\right) \qquad (3\text{-}5)$$

The region in which the function $\phi(i,j)$ is appreciably different from zero depends on the value of β. The volume of this region may be taken to be

$$V = 4\pi \int_0^\infty e^{-\beta^2 r^2} r^2 \, dr = \left(\frac{\sqrt{\pi}}{\beta}\right)^3 \qquad (3\text{-}6)$$

Colle and Salvetti assume that V is proportional to the volume of exclusion in Wigner's formula [57] with a proportionality constant k,

$$V = k \frac{1}{p(R)} \qquad (3\text{-}7)$$

so that

$$\beta = \sqrt{\pi} \left(\frac{p(R)}{k} \right)^{\frac{1}{3}} = q \cdot p^{\frac{1}{3}}(R) \qquad (3\text{-}8)$$

where q is constant, and from (3-8) we can see that

$$q = \sqrt{\pi} \left(\frac{1}{k} \right)^{\frac{1}{3}} \tag{3-9}$$

Colle and Salvetti empirically put q=2.29 [50] . It is clear that ß depends on the local density.

The second order density matrix for a two-electron system without spin may be written as [5]

$$P_2(121'2') = N(N-1) \cdot \int \Psi^{HF}(1,\ldots,N) \prod_{i<j} [1-\phi(ij)][1-\phi(i'j')] \Psi^{*\,HF}(1',2',3,\ldots,N) dr_3 \ldots dr_N ds_1 \ldots ds_N \tag{3-10}$$

where r_m and s_m represent the spatial and the spin coordinates of particles respectively. Because $\phi(12) << 1$ because of its exponential factor, we get approximately

$$P_2(121'2') = P_2^{HF}(121'2') \left(1-\phi(12)-\phi(1'2')+\phi(12)\phi(1'2')\right) \tag{3-11}$$

An assumption is made that

$$p_1(11') = p_1^{HF}(11') \tag{3-12}$$

where p_1 represents the first order density matrix. The formula (3-12) means the first-order density matrix of HF approximates well enough the exact first-order density matrix. From the N-representability of the reduced density matrices, we have

$$P_1(11') = \int P_2(121'2)\ d2 \qquad \text{(A)(3-13)}$$

$$P_1^{HF}(11') = \int P_2^{HF}(121'2)\ d2 \qquad \text{(B)(3-13)}$$

it follows

$$\int P_2(121'2)\ d2 = \int P_2^{HF}(121'2)\ d2 \qquad (3\text{-}14)$$

Combining this with (3-11) we have

$$\int P_2^{HF}(121'2')\cdot b(121'2')\ d2 = 0 \qquad (3\text{-}15)$$

where

$$b(121'2') = -\ \phi(12) - \phi(1'2') + \phi(12)\phi(1'2') \qquad (3\text{-}16)$$

Colle and Salvetti approximately solve the $\epsilon(R)$ from the equation (3-15) as

$$\epsilon(R) \approx \frac{\sqrt{\pi}\cdot\beta}{1 + \sqrt{\pi}\cdot\beta} \qquad (3\text{-}17)$$

Colle and Salvetti calculate Ec according to

$$Ec = E - E^{HF} = \tfrac{1}{2} \int P_2(12)\ (\phi'(12) - 2\phi(12))\ \frac{1}{r}\ d1\ d2 \tag{3-18}$$

This is the C-S theoretical formula.

Colle and Salvetti made a further simplification for the calculation of Ec. They proposed an empirical formula involving a Taylor expansion of P_2, so that the numerical integration only contains one variable R. The C-S numerical formula is

$$Ec = -0.04918 \int p(R)\ \frac{1 + 0.173\ W\ e^{(-0.58/\beta)}}{1 + 0.8/\beta}\ d\vec{R} \tag{3-19}$$

with

$$\beta = 2.29\ p^{\frac{1}{3}}(R) \tag{3-20}$$

$$W = 0.3814\ p^{\frac{-8}{3}}(R)\ \left[\ \nabla^2\ P_2(\vec{R} - \frac{\vec{r}}{2}\ ,\ \vec{R} + \frac{\vec{r}}{2})\ \right]_{r=0} \tag{3-21}$$

where ∇^2 will operate on r and is defined as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad \text{(A)(3-22)}$$

where

$$r^2 = x^2 + y^2 + z^2 \qquad (B)(3-23)$$

Colle and Salvetti listed the results of a number of ground state systems treated by the formula (3-19), which compared to the experimental values very well;the highest error reported is eight per cent of the correlation energy [50]. (Table 3.1)

The Colle and Salvetti ideas have been extended to calculate the excitation energy, ionization potentials and dissociation energies for some atoms and small molecules (Table 3.2) [58-60].

TABLE 3.1 THE CORRELATION ENERGY FOR SOME ATOMS AND SMALL MOLECULES calculated by Colle & Salvetti with comparing one by Clementi [50]

TRIAL	Ec (a.u.) COLLE-SALVETTI	Ec (a.u.) CLEMENTI	Error | % |
He	-0.0416	-0.0420	1.0
Li^+	-0.0438	-0.0435	0.7
Be^{2+}	-0.0441	-0.0443	0.4
Be	-0.0926	-0.0940	1.5
B^+	-0.106	-0.1123	5.4
Ne	-0.374	-0.372	0.5
CH_4	-0.289	-0.283	2.1
H_2O	-0.336	-0.364	7.7

TABLE 3.2 THE EXCITATION ENERGY, IONIZATION POTENTIAL, DISSOCIATION ENERGY CALCULATED BY COLLE & SALVETTI WITH THEIR NUMERICAL FORMULA [58] AND ADD TO THE HF OR THE MC-SCF VALUES COMPARED TO THE EXACT VALUES [3]

SYSTEM			ΔE (ev) COLLE-SALVETTI	ΔE (ev) EXACT
Be	^1S	$(2s \rightarrow 3s)$	6.7	6.8
	^1S	$(2s \rightarrow 4s)$	8.1	8.1
C_2H_4	$^1B_1$	$(1b_3 \rightarrow 1b_2)$	7.8	7.66
CH_2O	$^1B_2$	$(2b_2 \rightarrow 6a_1)$	7.14	7.10
	$^1B_2$	$(2b_2 \rightarrow 7a_1)$	8.02	8.14
	$^1B_2$	$(2b_2 \rightarrow 8a_1)$	8.96	9.24
	$^1B_2$	$(2b_2 \rightarrow 9a_1)$	9.30	9.62
	$^2B_3$	Ionization Potential	10.65	10.88
H_2	$X^1\Sigma^+$	Dissociation Energy	4.72	4.75

(B). Calculation of the correlation energy for three series of Isoelectronic Ions

The Colle-Salvetti numerical formula (3-19) and their functional (3-17) are tested by calculating the correlation energy Ec of He, Be, Ne atoms, as well as the corresponding isoelectronic series with a single determinant of the HF orbitals [61]. The details of the formulas used in the calculation are shown in Appendix 2.

Also the calculations of Ec are performed with the formula (3-18),by using our program of 3 Dimensional Simpson Numerical Integration (3D SI) and same HF orbitals. The correlation function $\phi(i,j)$ and the $\epsilon(R)$ were taken from the formula (3-3) and (3-17) which are used by Colle-Salvetti.

The results are compared with ones of Ab initio calculations from Clementi [3] as a reference, which are considered to be accurate correlation energies. These are shown in Table 3.3 to 3.5 with Figure 2.1 to 2.3 respectively. We see that the results of only some trials from the Colle-Salvetti numerical formula are close to those from Clementi. By increasing the nuclear charge Z the results go far from the Clementi results.

TABLE 3.3 THE CORRELATION ENERGY OF He ISOELECTRONIC SERIES CALCULATED BY 3D SI WITH FORMULA $\frac{1}{2}\langle P_2 b/r\rangle$ AND COMPARED ONE FROM C-S NUMERICAL FORMULA AND ONE FROM CLEMENTI

Z	SYSTEM	C-S NUMERICAL (a.u.)	CLEMENTI (a.u.)	FORMULA $\frac{1}{2}\langle P_2 b/r\rangle$ BY 3D SI (a.u.)
Z=2	He	-0.0420	-0.0421	-0.0423
Z=3	Li^{+1}	-0.0441	-0.0435	-0.0491
Z=4	Be^{+2}	-0.0442	-0.0443	-0.0531
Z=5	B^{+3}	-0.0438	-0.0448	-0.0557
Z=6	C^{+4}	-0.0432	-0.0451	-0.0575
Z=7	N^{+5}	-0.0426	-0.0453	-0.0590
Z=8	O^{+6}	-0.0419	-0.0455	-0.0600
Z=9	F^{+7}	-0.0413	-0.0456	-0.0608
Z=10	Ne^{+8}	-0.0406	-0.0457	-0.0615
Z=11	Na^{+9}	-0.0400	-0.0458	-0.0621
Z=12	Mg^{+10}	-0.0394	-0.0459	-0.0626
Z=13	Al^{+11}	-0.0389	-0.0459	-0.0630
Z=14	Si^{+12}	-0.0384	-0.0460	-0.0634
Z=15	P^{+13}	-0.0379	-0.0461	-0.0637
Z=16	S^{+14}	-0.0375	-0.0461	-0.0639
Z=17	Cl^{+15}	-0.0370	-0.0462	-0.0641
Z=18	Ar^{+16}	-0.0367	-0.0463	-0.0643
Z=19	K^{+17}	-0.0363	-0.0463	-0.0645
Z=20	Ca^{+18}	-0.0359	-0.0463	-0.0647
Z=21	Sc^{+19}	-0.0356	-0.046	-0.0648
Z=22	Ti^{+20}	-0.0353	-0.046	-0.0650
Z=23	V^{+21}	-0.0350	-0.047	-0.0651
Z=24	Cr^{+22}	-0.0347	-0.047	-0.0652
Z=25	Mn^{+23}	-0.0344	-0.047	-0.0653
Z=26	Fe^{+24}	-0.0341	-0.047	-0.0654
Z=27	Co^{+25}	-0.0339	-0.047	-0.0655
Z=28	Ni^{+26}	-0.0336	-0.047	-0.0656
Z=29	Cu^{+27}	-0.0334	-0.047	-0.0657
Z=30	Zn^{+28}	-0.0332	-0.047	-0.0658
Z=31	Ga^{+29}	-0.0330	-0.047	-0.0659
Z=32	Ge^{+30}	-0.0327	-0.047	-0.0659
Z=33	As^{+31}	-0.0326	-0.047	-0.0659
Z=34	Se^{+32}	-0.0324	-0.047	-0.0660
Z=35	Br^{+33}	-0.0322	-0.047	-0.0661
Z=36	Kr^{+34}	-0.0320	-0.047	-0.0661

Figure 2.1 A COMPARISON OF Ec

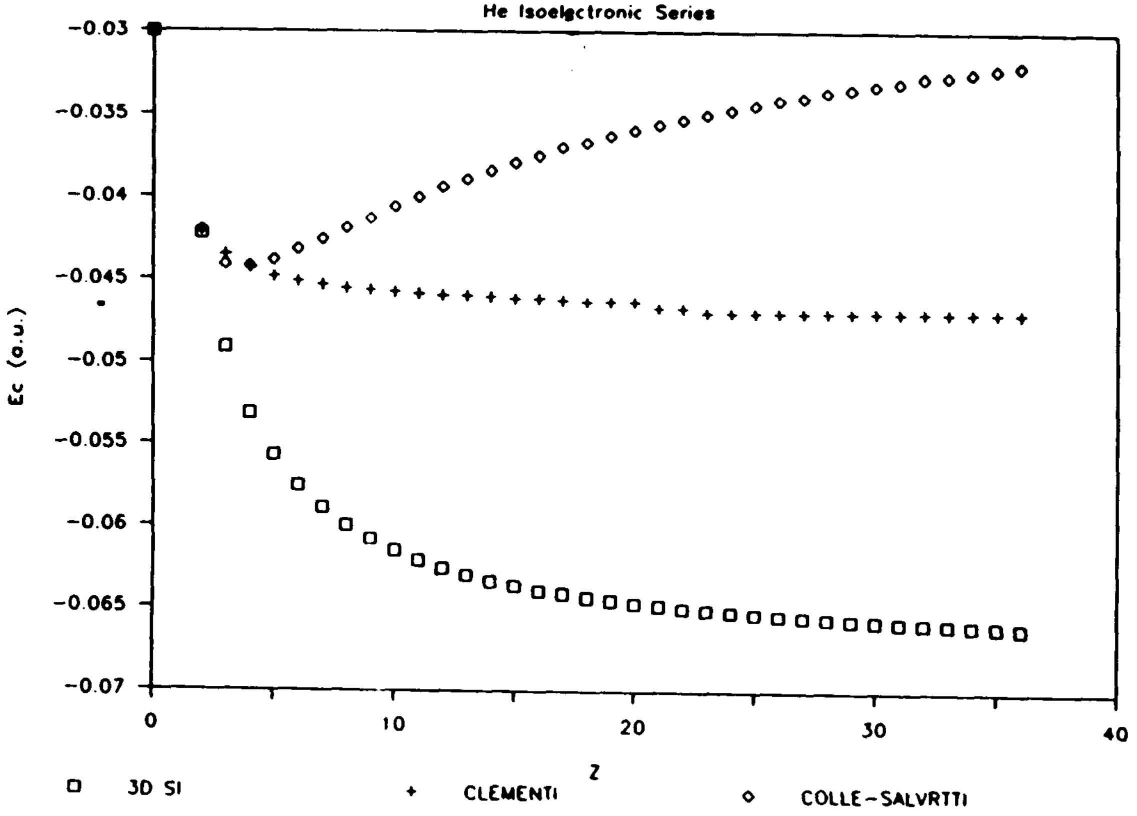


TABLE 3.4 THE CORRELATION ENERGY OF Be ISOELECTRONIC SERIES CALCULATED BY 3D SI WITH FORMULA $\frac{1}{2}<P_2b/r>$ AND COMPARED ONE FROM C-S NUMERICAL FORMULA AND ONE FROM CLEMENTI

Z	SYSTEM	C-S NUMERICAL (a.u.)	CLEMENTI (a.u.)	FORMULA $\frac{1}{2}<P_2b/r>$ BY 3D SI (a.u.)
Z=4	Be	-0.0932	-0.0944	-0.0585
Z=5	B^{+1}	-0.1060	-0.1123	-0.0700
Z=6	C^{+2}	-0.1163	-0.1268	-0.0771
Z=7	N^{+3}	-0.1270	-0.1412	-0.0808
Z=8	O^{+4}	-0.1281	-0.1551	-0.0846
Z=9	F^{+5}	-0.1312	-0.1684	-0.0891
Z=10	Ne^{+6}	-0.1332	-0.1814	-0.0936
Z=11	Na^{+7}	-0.1348	-0.1941	-0.0969
Z=12	Mg^{+8}	-0.1360	-0.2066	-0.0995
Z=13	Al^{+9}	-0.1372	-0.2190	-0.1014
Z=14	Si^{+10}	-0.1380	-0.2313	-0.1029
Z=15	P^{+11}	-0.1392	-0.2435	-0.1042
Z=16	S^{+12}	-0.1402	-0.2556	-0.1053
Z=17	Cl^{+13}	-0.1410	-0.2677	-0.1062
Z=18	Ar^{+14}	-0.1417	-0.2797	-0.1070
Z=19	K^{+15}	-0.1406	-0.2917	-0.1078
Z=20	Ca^{+16}	-0.1425	-0.3037	-0.1086
Z=21	Sc^{+17}	-0.1428	-0.316	-0.1092
Z=22	Ti^{+18}	-0.1431	-0.327	-0.1098
Z=23	V^{+19}	-0.1433	-0.339	-0.1104
Z=24	Cr^{+20}	-0.1435	-0.351	-0.1109
Z=25	Mn^{+21}	-0.1437	-0.363	-0.1114
Z=26	Fe^{+22}	-0.1438	-0.375	-0.1118
Z=27	Co^{+23}	-0.1439	-0.387	-0.1122
Z=28	Ni^{+24}	-0.1440	-0.398	-0.1126
Z=29	Cu^{+25}	-0.1440	-0.411	-0.1130
Z=30	Zn^{+26}	-0.1441	-0.423	-0.1133
Z=31	Ga^{+27}	-0.1441	-0.434	-0.1136
Z=32	Ge^{+28}	-0.1441	-0.446	-0.1149
Z=33	As^{+29}	-0.1441	-0.458	-0.1142
Z=34	Se^{+30}	-0.1441	-0.470	-0.1144
Z=35	Br^{+31}	-0.1440	-0.482	-0.1147
Z=36	Kr^{+32}	-0.1440	-0.494	-0.1149

Figure 2.2 A COMPARISON OF Ec

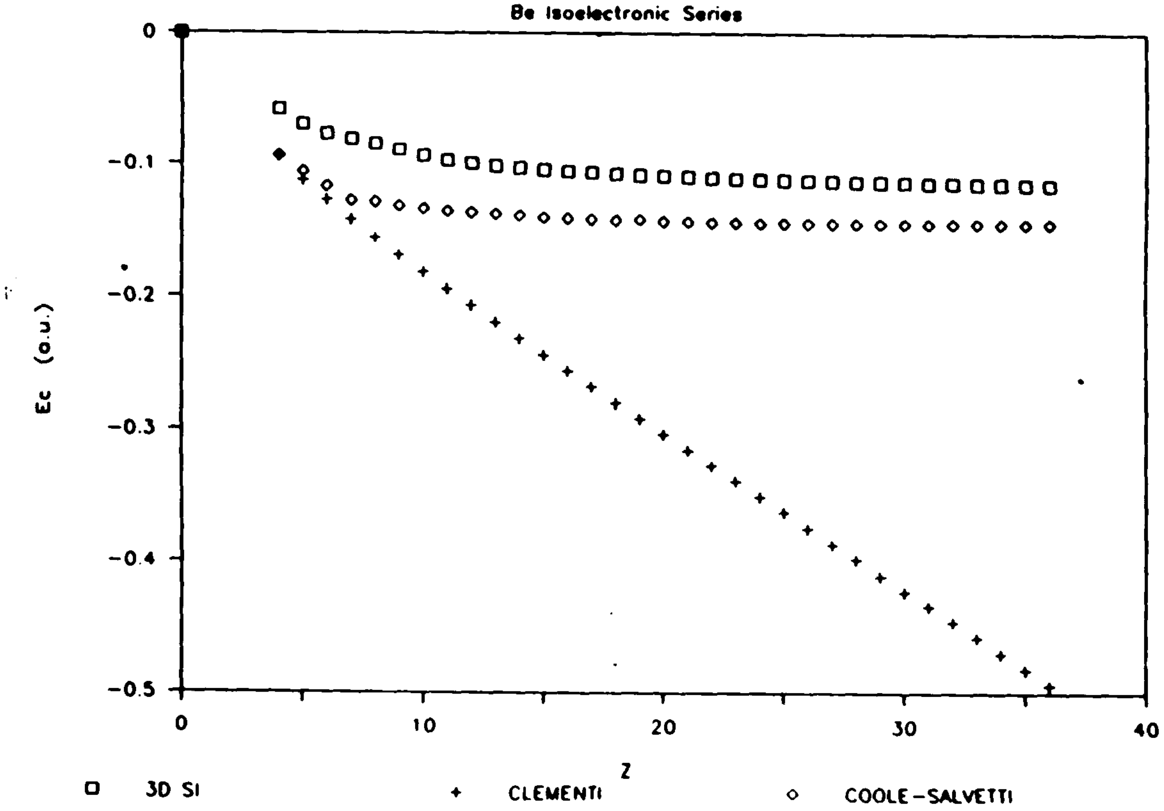
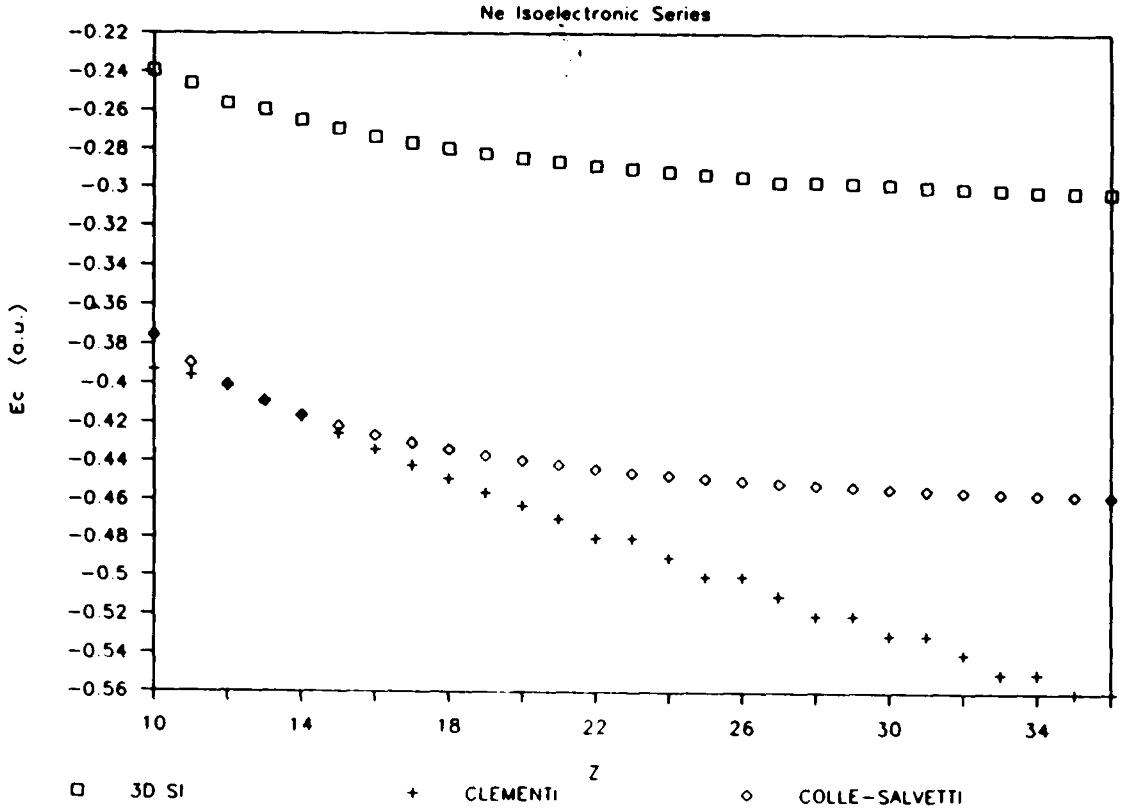


TABLE 3.5 THE CORRELATION ENERGY OF Ne ISOELECTRONIC SERIES CALCULATED BY 3D SI WITH FORMULA $\frac{1}{4}\langle P_2 b/r\rangle$ AND COMPARED ONE FROM C-S NUMERICAL FORMULA AND ONE FROM CLEMENTI

Z	SYSTEM	C-S NUMERICAL (a.u.)	CLEMENTI (a.u.)	FORMULA $\frac{1}{4}\langle P_2 b/r\rangle$ BY 3D SI (a.u.)
Z=10	Ne	-0.375	-0.393	-0.0423
Z=11	Na^{+1}	-0.390	-0.396	-0.0491
Z=12	Mg^{+2}	-0.401	-0.402	-0.0531
Z=13	Al^{+3}	-0.409	-0.409	-0.0557
Z=14	Si^{+4}	-0.416	-0.417	-0.0575
Z=15	P^{+5}	-0.422	-0.426	-0.0590
Z=16	S^{+6}	-0.427	-0.434	-0.0600
Z=17	Cl^{+7}	-0.431	-0.442	-0.0608
Z=18	Ar^{+8}	-0.434	-0.449	-0.0615
Z=19	K^{+9}	-0.437	-0.456	-0.0621
Z=20	Ca^{+10}	-0.440	-0.463	-0.0626
Z=21	Sc^{+11}	-0.442	-0.47	-0.0630
Z=22	Ti^{+12}	-0.444	-0.48	-0.0634
Z=23	V^{+13}	-0.446	-0.48	-0.0637
Z=24	Cr^{+14}	-0.447	-0.49	-0.0639
Z=25	Mn^{+15}	-0.449	-0.50	-0.0641
Z=26	Fe^{+16}	-0.450	-0.50	-0.0643
Z=27	Co^{+17}	-0.451	-0.51	-0.0645
Z=28	Ni^{+18}	-0.452	-0.52	-0.0647
Z=29	Cu^{+19}	-0.453	-0.52	-0.0648
Z=30	Zn^{+20}	-0.454	-0.53	-0.0650
Z=31	Ga^{+21}	-0.455	-0.53	-0.0651
Z=32	Ge^{+22}	-0.456	-0.54	-0.0652
Z=33	As^{+23}	-0.456	-0.55	-0.0653
Z=34	Se^{+24}	-0.457	-0.55	-0.0654
Z=35	Br^{+25}	-0.457	-0.56	-0.0655
Z=36	Kr^{+26}	-0.458	-0.56	-0.0656

Figure 2.3 A COMPARISON OF Ec



(C). REMARKS ON THE COLLE-SALVETTI FORMALISM

Three groups of the results of the correlation energy are compared in Table 3.3, 3.4 ,3.5 and Figure 2.1,2.2,2.3. The first is from our calculations with the Colle-Salvetti numerical formula (3-19); the second group is calculated by Clementi which is a standard reference; and the last group is from the calculation with the formula (3-18) and our 3 dimensional Simpson integration (3D SI). Most results are far away from the Clementi results, which are considered to be nearly exact. It is clear that the Colle-Salvetti numerical formalism (3-19) introduced several constants which depend on a empirical fitting procedure, does give some results close to the Clementi results.

Considerations of with the Colle and Salvetti formalism are given below:

<1> As a consequence of their approximations, the density matrices derived from correlated wavefunction are not N-representable. Cohen, Santhanam and Frishberg [62] have argued that when a second-order density matrix is approximated by a N-representable part plus a non N-representable component, the resultant density matrix might still be reasonable if the non N-representable part is small. In Colle-Salvetti two-body density matrix, only the Hartree-Fock density matrix is N-representable, the non N-representability is introduced by the approximations of adding a correlation part as a small contribution.

There has been a study of the Colle-Salvetti formula substituting for the HF determinant a determinant of X-ray orbitals, which delivers the exact density in the article of Cohen, Frishberg, Lee and Massa [63]. The Be atom was a trial for a test calculation with Colle-Salvetti numerical formula (3-19) by Cohen et al. The result Ec = -0.093618 a.u., is very close to the result from Veillard and Clementi by less than 2% [4].

<2> The two body Hamiltonian usually has a form

$$H = \Sigma h_i + \Sigma h_{ij} \qquad (3\text{-}25)$$

where

$$h_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \qquad (A)(3\text{-}26)$$

$$h_{ij} = \frac{1}{r_{ij}} \qquad (B)(3\text{-}26)$$

Then, the expectation value of H for the two-body case is

$$E = \int h_1 p\,(11')\Big|_{1'\to 1} d1 + \frac{1}{2} \int h_{12} P_2(12)\; d1\; d2 \qquad (3\text{-}27)$$

The terms of the usual Hamiltonian in general should all contribute to the total correlation energy Ec. But in the Colle-Salvetti formalism only the term with h_{ij} contributes They assume Hartree-Fock one-body density matrix to be equal to the exact one-body density matrix as in equation (3-12). This assumption is consistent with

$$I = \int P_2(12)\ (\phi^2(12) - 2\phi(12))\ d1\ d2 = 0 \tag{3-28}$$

In the C-S approximation one may neglect the contribution from some terms in the kinetic and potential energy to Ec. For example, the correlation from the electron-nuclear attraction has been neglected

$$\begin{aligned} Vc(2) &= -Z \int b(12)\ \frac{1}{r_1}\ P_2(12)\ \ d1\ d2 \\ &= \int \frac{-Z}{r_1}\ d1 \int b(12) \cdot P_2(12)\ d2 = 0 \end{aligned} \tag{3-29}$$

Although neglected in the Colle-Salvetti case is in general not zero.

<3> The functional $\epsilon(R)$ (3-17) of C-S formalism does not satisfy the original equation (3-15), so that the "I" values in (3-28) and Vc(2) in (3-29) can be different from zero. Calculations of I values and Vc(2) with the functional $\epsilon(R)$ of (3-17) are performed by 3D SI program. The results from different q values are listed on the Table 3.6 and the Table 3.7. When q=2.29 which is the value taken by Colle-Salvetti, for the He atom I= -0.0242 a.u. and Vc(2) = 0.0621 a.u., the exact Ec is -0.042 a.u. for He atom. Notice that the

magnitude of I is large compared to the value of Ec.

<4> The normalization of the density is exact if (3-15) holds exactly. The normalization of the density is then given by

$$\int p_1(11')\Big|_{1'\to 1} d1 = \int p_1^{HF}(11')\Big|_{1'\to 1} d1 = N \qquad (3\text{-}30)$$

TABLE 3.6 $\langle b\cdot P_2\rangle$ OF He ATOM CALCULATED BY 3D SI WITH THE C-S FUNCTIONAL

$$\epsilon(R) = \frac{\sqrt{\pi}\cdot\beta}{1+\sqrt{\pi}\beta}$$

q	$\langle b\cdot P_2\rangle$	q	$\langle b\cdot P_2\rangle$
0.69	-0.6880	1.69	-0.0758
0.79	-0.5515	1.79	-0.0619
0.89	-0.4405	1.89	-0.0508
0.99	-0.3512	1.99	-0.0418
1.09	-0.2800	2.09	-0.0347
1.19	-0.2235	2.19	-0.0289
1.29	-0.1788	2.29	-0.0242
1.39	-0.1434	2.39	-0.0203
1.49	-0.1155	2.49	-0.0172
1.59	-0.0933		

Figure 2.4 A CALCULATION <b*P2> OF He

BY 3D SI WITH COLLE-SALVETTI FUNCTIONAL

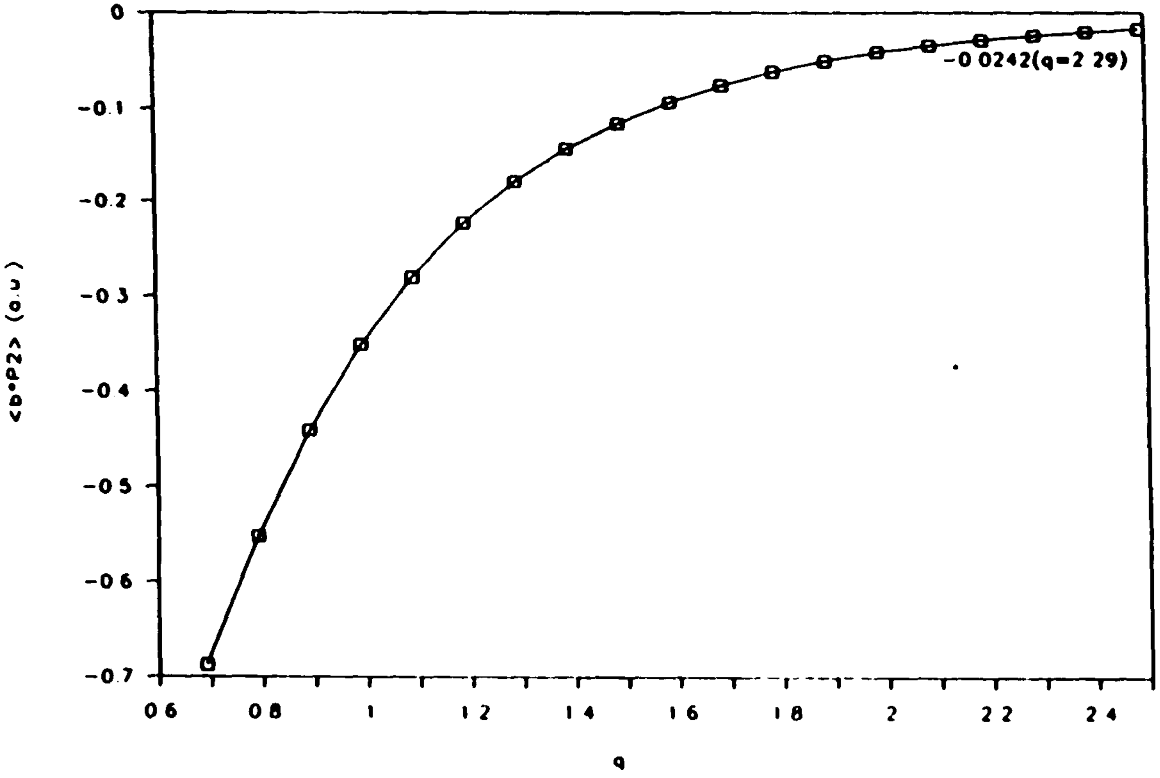


TABLE 3.7 $-Z <b \cdot P_2/r_1>$ OF He ATOM CALCULATED BY 3D SI WITH COLLE-SALVETTI FUNCTIONAL

$$\epsilon(R) = \frac{\sqrt{\pi} \cdot \beta}{1 + \sqrt{\pi}\beta}$$

q	$-Z<b \cdot P_2/r_1>$	q	$-Z<b \cdot P_2/r_1>$
0.69	2.3816	0.79	1.9018
0.89	1.5076	0.99	1.1889
1.09	0.9342	1.19	0.7327
1.29	0.5744	1.39	0.4507
1.49	0.3545	1.59	0.2797
1.69	0.2217	1.79	0.1766
1.89	0.1414	1.99	0.1140
2.09	0.0925	2.29	0.0621

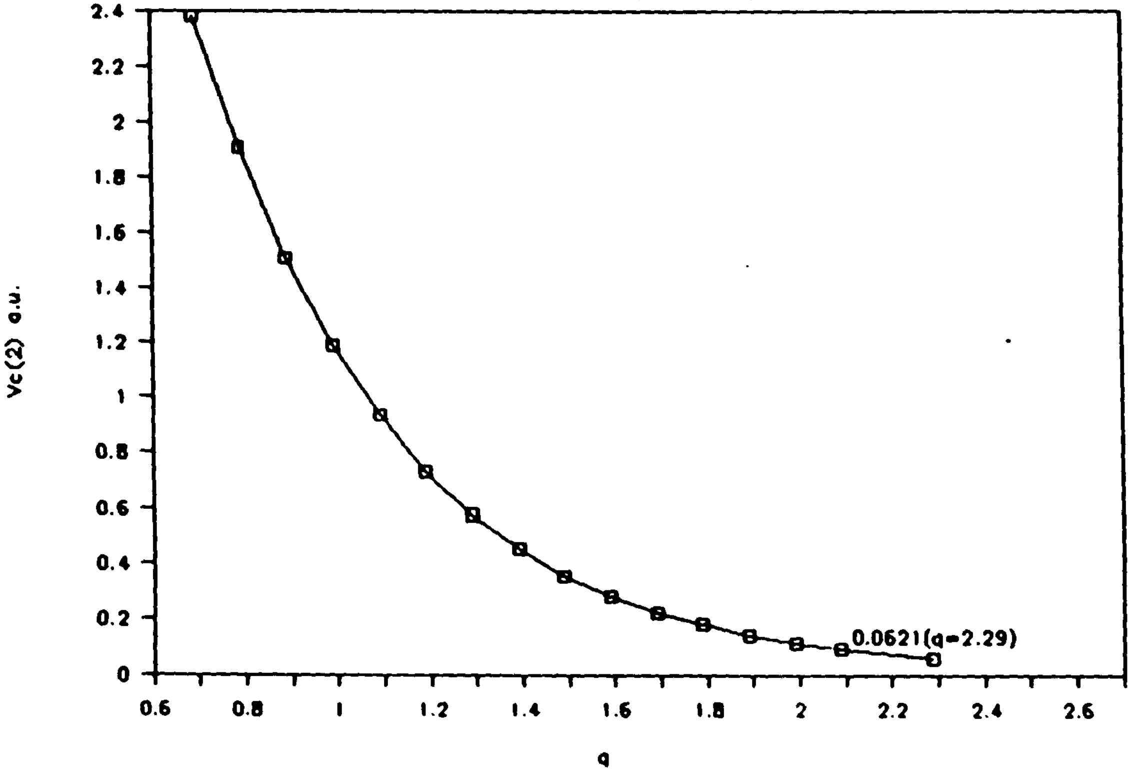


Figure 2.5 A CALCULATION Vc(2) OF He

BY 3D SI WITH COLLE-SALVETTI FUNCTIONAL

CHAPTER IV A FORMALISM FOR CORRELATION ENERGY

In this chapter, a formalism for correlation energy [5] is considered with:

<1> Highly accurate approximately N-representable density matrices from a single determinant wave function, which is constructed with HF orbitals.

<2> Correlation contributions from both kinetic and potential energy.

<3> A functional $\epsilon(R)$ which ensures normalization of the wave function.

This new formalism leads to a procedure which applies our 3 Dimensional Simpson Integration (3D SI) computer program to calculate the correlation energy of a close-shell system without any approximate Taylor expansion. Testing of the correlation energy for He and its isoelectronic ions has been performed. The results have reached about 70% of the exact Ec value. The optimum values of variational parameters giving Ec for the He isoelectronic series have been found. The percentage correlation contribution of each term in Ec have been determined. All of our results give reasonable values with clear physical meaning and support our theoretical picture of correlation.

(A) DERIVATION OF THE REDUCED DENSITY MATRICES

In this thesis the N-representability of density matrices is ensured, since this is required by quantum mechanics [62]. The problem of N-representability is that of finding conditions by which to recognize the reduced density matrices which are related to an N-body wave function according to the rule (4-1)

$$Pm(1,\ldots,N,1',\ldots,N') = N(N-1)\ldots(N-m+1) \int \Psi\Psi^{*}\, dm+1\ldots dN \tag{4-1}$$

where Ψ is an antisymmetric N-body wavefunction.

For convenience $p_1(ij')$ or $p(ij')$ represent a first order density matrix, and $P_2(iji'j')$ represents a second order density matrix.

All higher order density matrices are known functionals of first order density matrices in the single determinant case. The diagonal elements of p(11') delivers by the density itself

$$p(1) = p(11') \Big|_{1'\to 1} \tag{4-2}$$

Furthermore, it occurs by Gilbert's theorem [45] that any normalized, well behaved density is N-representable by a single Slater determinant of orbitals. The density matrices

$P_{1det}(11')$, are N-representable by a single Slater determinant Ψ_{det} , ie,

$$\Psi_{det}(1,\ldots,N) = \frac{1}{N!}\begin{vmatrix} \Phi_1(1)\ldots & \Phi_1(N) \\ \vdots & \vdots \\ \Phi_N(1)\ldots & \Phi_N(N) \end{vmatrix} \qquad (4\text{-}3)$$

and

$$\Phi_m = \Sigma\, C_k \Omega_k \qquad (4\text{-}4)$$

where Ω_k is a basis, and the population matrix $\underset{\sim}{P}$ is

$$\underset{\sim}{P} = \underset{\sim}{C}^+\underset{\sim}{C} \qquad (4\text{-}5)$$

The population matrix $\underset{\sim}{P}$ is required to be a Hermitian, normalized projector and satisfies the experimental scattering factors [32], ie.,

$$\underset{\sim}{P} = \underset{\sim}{P}^+ \qquad (A)\,(4\text{-}6)$$

$$\mathrm{tr}\ \underset{\sim}{P} = N \qquad (B)\,(4\text{-}6)$$

$$\underset{\sim}{P}^2 = \underset{\sim}{P} \qquad (C)\,(4\text{-}6)$$

$$F(\vec{k}) = \mathrm{tr}\ \underline{P}\ \underline{f}(\vec{k}) \qquad \text{(D)(4-6)}$$

If the $\underline{P}$ matrix is a solution of Clinton's equation, the above conditions should be satisfied. Clinton's equation is

$$\underline{P}_{n+1} = 3\ \underline{P}_n^2 - 2\ \underline{P}_n^3 + \lambda_K\ \underline{f}(k) + \lambda_N\ \underline{1} \qquad (1\text{-}48)$$

where λ_K and λ_N are Lagrangian multipliers. So

$$P_{1\underline{det}}(11') = \mathrm{tr}\ \underline{P}\ \underline{\Omega}(1)^{+}\underline{\Omega}\ (1') \qquad (4\text{-}8)$$

will be single determinant N-representable, and have diagonal elements which deliver the experimental density [47] i.e.,

$$p(1) = P_{1\underline{det}}(11')\Big|_{1'\to 1} = \mathrm{tr}\ \underline{P}\ \underline{\Omega}(1)\ \underline{\Omega}^{+}(1) \qquad (4\text{-}9)$$

A highly accurate wavefunction can be generated by the product of the above determinant wavefunction and a spinless symmetric correlation function [16,62,63]

$$\Psi = \Psi_{\underline{det}}(1,\ldots,N) \prod_{i>j} [1-\phi(ij)] \qquad (4\text{-}10)$$

The correlation function $\phi(i,j)$ is defined symmetric to permutation in the coordinates of particle pairs so that the total wave function of (4-10) is antisymmetric as required. The density matrices which flow from correlated determinant wave functions (4-10), may be obtained by integration directly from the fundamental definition (4-1) of density matrices, and contain a finite number of expansion terms in the form [64]

$$p(11') = p^{(0)}(11') + p^{(1)}(11') + p^{(2)}(11') + \ldots + p^{\frac{N(N-1)}{2}}(11') \qquad \text{(A)(4-11)}$$

$$p_2(12) = p_2^{(0)}(12) + p_2^{(1)}(12) + p_2^{(2)}(12) + \ldots + p_2^{\frac{N(N-1)}{2}}(12) \qquad \text{(B)(4-11)}$$

For convenience define b(iji'j') as

$$b(iji'j') = -\phi(ij) - \phi(i'j') + \phi(ij)\cdot\phi(i'j') \qquad (4\text{-}12)$$

The properties of the system are expected to be calculated to be accurately enough up to second order in these terms because of the general smallness of the b(iji'j'). Since the Hamiltonian contains only one and two-body terms usually, the reduction from an N-body to a two-body description occurs [5]. Within this analysis for a two body system the density matrices are obtained as

$$P_2(121'2') = P_{2\underline{det}}(121'2') + P_{2\underline{det}}(121'2')\cdot b(121'2') \qquad (4\text{-}13)$$

These highly accurate density matrices are approximately N-representable.

From (4-1) we have

$$p_1(11') = \frac{1}{N-1} \int P_2(121'2)\ d2 \qquad (4-14)$$

From (4-13) and (4-14), $P_1(11')$ could be

$$p_1(11') = p_{1\underline{det}}(11') + \int P_{2\underline{det}}(121'2)\cdot b(121'2)\ d2$$

$$(4-15)$$

The above density matrices are approximately N-representable, and may be used to calculate the correlation energy. The Hohenberg and Kohn (HK) theorem [25] states that the many-particle ground state is a unique functional of the electronic density, this means that the electron density which can be used to determine the above density matrices, contains all the information necessary to evaluate every electronic property of the system.

(B) DERIVATION OF A CORRELATION ENERGY FORMULA

The two body Hamiltonian has the usual form

$$H = \Sigma\, h_i + \Sigma\, h_{ij} \qquad (4-16)$$

where

$$h_i = -\tfrac{1}{2}\,\nabla_i^2 - \frac{Z}{r_i} \qquad (A)(4-17)$$

$$h_{ij} = \frac{1}{r_{ij}} \qquad \text{(B)(4-17)}$$

From the HK theorem, the expectation value of H for two bodies is

$$E = \int h_1 p\,(11')\Big|_{1'\rightarrow 1} d1 + \tfrac{1}{2}\int h_{12}P_2(12)\;d1\;d2 \qquad (4\text{-}18)$$

The correlation energy is calculated using the exact density determinant as

$$Ec = E_{exa} - E_{\underline{det}} \qquad (4\text{-}19)$$

where

$$E_{\underline{det}} = \int h_1 p_{1\underline{det}}(11')\Big|_{1'\rightarrow 1} d1 + \tfrac{1}{2}\int h_{12}P_{2\underline{det}}(12)\;d1\;d2 \qquad (4\text{-}20)$$

where ∇ operates on r_1 ie,

$$\nabla^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \qquad \text{(A)(4-21)}$$

$$r_1^2 = x_1^2 + y_1^2 + z_1^2 \qquad \text{(B)(4-21)}$$

From (4-15), (4-18) and (4-20) we have

$$Ec = -\tfrac{1}{2} \int \nabla^2 \left(b(121'2) \cdot P_{2\underline{det}}(121'2)\right) \Big|_{1' \to 1} d1\ d2$$

$$- Z \int b(12) \cdot P_{2\underline{det}}(12) \frac{1}{r_1} d1\ d2$$

$$+ \tfrac{1}{2} \int b(12) \cdot P_{2\underline{det}}(12) \frac{1}{r} d1\ d2 \qquad (4\text{-}22)$$

where

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$= \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} \qquad (4\text{-}23)$$

For convenience, we list definitions

$$Vc(1) = \tfrac{1}{2} \int b(12) \cdot P_{2\underline{det}}(12) \frac{1}{r} d1\ d2 \qquad (A)(4\text{-}24)$$

$$Vc(2) = - \int b(12) \cdot P_{2\underline{det}}(12) \frac{Z}{r_1} d1\ d2 \qquad (B)(4\text{-}24)$$

$$Tc(1) = - \tfrac{1}{2} \int b(121'2) \cdot \nabla^2 P_{2\underline{det}}(121'2) \Big|_{1' \to 1} d1\ d2 \qquad (C)(4\text{-}24)$$

$$Tc(2) = - \int \nabla b(121'2) \cdot \nabla P_{2\underline{det}}(121'2) \Big|_{1' \to 1} d1\ d2 \qquad (D)(4\text{-}24)$$

$$Tc(3) = -\tfrac{1}{2}\int P_{2\underline{det}}(121'2)\cdot\nabla^2 b(121'2)\Big|_{1'\to 1} d1\, d2 \qquad \text{(E)(4-24)}$$

The correlation function form is taken as [2]

$$\phi(12) = e^{-\beta^2 r^2}\left[\, 1 - \epsilon(R)\ \left(1+ \frac{r}{2} \right) \right] \qquad (4\text{-}25)$$

where

$$\vec{R} = \tfrac{1}{2}\ (\vec{r}_1 + \vec{r}_2) \qquad \text{(A)(4-26)}$$

$$R = \frac{1}{4}\sqrt{(x_1+x_2)^2 + (y_1+y_2)^2 + (z_1+z_2)^2} \qquad \text{(B)(4-26)}$$

$$\vec{r} = (\vec{r}_1 - \vec{r}_2) \qquad \text{(C)(4-26)}$$

$$r = \sqrt{(x_1-x_2)^2 + (y_1-y_2)^2 + (z_1-z_2)^2} \qquad \text{(D)(4-26)}$$

The definition of $\phi(12)$ fulfills all the conditions of the cusp for $r_1 \to r_2$ [56]. From (4-10) and (4-25), it is clear when the electrons are far apart the wave function (4-10) is reduced to the single determinant, and when a pair of electrons collide the function $\phi(12)$ becomes

$$\Psi = \Psi_{\underline{det}}\ \epsilon(R) \qquad (4\text{-}27)$$

The region in which the function $\phi(12)$ is appreciably different from zero depends on the value of β. the volume of this region may be taken to be

$$V = 4\pi \int e^{-\beta^2 r^2} r^2 \, dr = \left(\frac{\sqrt{\pi}}{\beta} \right)^3 \qquad (4\text{-}28)$$

For reasonable β value a assumption is made as that the volume V in (4-28) should be proportional to the volume of exclusion in Wigner's formula [57]. So we have

$$V = k \, \frac{1}{p(R)} \qquad (4\text{-}29)$$

where p(R) is the electronic density and k is proportional constant. This formula indicates the physical meaning of k, which is the average number of the electrons in volume V. From (4-28) and (4-29) we have

$$\beta = \sqrt{\pi} \cdot k^{-1/3} p(R)^{1/3} = q \cdot p(R)^{1/3} \qquad (4\text{-}30)$$

where

$$q = \sqrt{\pi} \cdot k^{-1/3} \qquad (4\text{-}31)$$

For the He atom and its isoelectronic series each trial has 2 electrons, so $k \leq 2$. we assume the average number in V is equal to 2 for He and its series, so q should be

$$q(\mathrm{He}) \geq \sqrt{\pi}\cdot 2^{-1/3} \approx 1.4068 \qquad (4\text{-}32)$$

Also the q can be considered a parameter, finding the optimum value of Ec.

The functional $\epsilon(R)$ should be consistent with the density normalization, ie,

$$\int P_{1\underline{exact}}(11')\Big|_{1'\to 1} d1 = \int P_{1\underline{det}}(11)\Big|_{1'\to 1} d1 = N \qquad (4\text{-}33)$$

For the He isoelectronic series N = 2. From equation (4-15)

$$I = \int b(12)\ P_{2\underline{det}}(12)\ d2\ d1 = 0 \qquad (4\text{-}34)$$

The functional $\epsilon(R)$ should satisfy the equation (4-34), for density normalization. In general all terms of the correlation energy from the usual Hamiltonian contribute to Ec. Here Tc(1), Tc(2), Tc(3), Vc(1) and Vc(2) all have contributions to Ec. The Colle-Salvetti formalism does not require the terms Tc(1) and Vc(2), which here contribute to the total correlation energy.

In this thesis the form of $\epsilon(R)$ is introduced as

$$\epsilon(R) = \frac{u\sqrt{\pi}\cdot\beta}{t + \sqrt{\pi}\cdot\beta} \qquad (4\text{-}35)$$

This formula is inspired by the formula of Colle-Salvetti, and its use make easy satisfaction the equation of normalization in (4-34) by adjustment of the parameter t. The variational parameter u in (4-35) is introduced to obtain greater flexibility in optimizing Ec.

(C) THE CALCULATIONS OF CORRELATION ENERGY

All of the numerical integrations are performed by our 3D SI program without any approximate series expansions. There are two ways for determining q. One way is by taking q = 1.4068 which is its value in (4-32) for the He isoelectronic series. That means we assume the average electronic number in the region, in which the function $\phi(12)$ is appreciably different from zero, is equal to total number of the electrons in the system. Another is to take q as a variational parameter and let both q and u change in order to bring Ec to its best value at the minimum of Ec.

A summary of the procedure follows:

<1> Take a u value u_i and find a t value $t_0(i)$, which satisfies the equation (4-34) under this u_i by the premium selection method in mathematics. The u_i value should be limited by $t \geq 0$. This premium selection process may be completed by a computer program automatically.

<2> Use both u_i and $t_0(i)$ values to calculate the correlation energy Ec(i) by the equations (4-22).

<3> Repeat above steps <1> and <2> to get more values of correlation energy Ec(i+1),Ec(i+2) ... under different u_{i+1}, u_{i+2}... and $t_0(i+1)$, $t_0(i+2)$ ... values.

<4> The values of Ec are plotted vs. u, then take the minimum of Ec.

<5> The parameter q may be varied similarly to u . It is not necessary just take q =1.4068, although this value consistent with Colle and Salvetti formalism. The double parameters u and q can be varied to find the minimum of Ec as the best value, which of cause will give better values, when only a single parameter u is varied.

When q = 1.4068 and the u parameter is varied, the results of the calculations for He, Li^+, Be^{+2} and B^{+3} are listed in the Table (4.1),the Table (4.2) and Figure 4.1(A) to 4.5(B). The computer program's zero for Epsilon is Epsilon ≤ 0.00001 in the calculations. The results showed over 50% of correlation energy have been recovered.

The Ec of He, Li^+ and Be^+2 are calculated by varying both parameter u and q. The results have reached about 70% of the exact value and are listed in Table 4.3 and Figures 4.6A to 4.7B. These results strongly support our formalism.

TABLE 4.1A THE CORRELATION ENERGY OF He ATOM CALCULATED BY VARYING THE u PARAMETER (q = 1.4068)

He u	t	Tc	Vc(1)/Vc(2)	Vc	Ec
0.90	0.4829350	0.0100	-0.0595 0.0289	-0.0306	-0.0206
0.94	0.5698257	0.0319	-0.0554 0.0020	-0.0534	-0.0216
0.95	0.5920193	0.0368	-0.0545 -0.0038	-0.0585	-0.0217
0.96	0.6128494	0.0428	-0.0532 -0.1213	-0.0653	-0.0226
0.97	0.6350412	0.0476	-0.0523 -0.0178	-0.0702	-0.0226
0.98	0.6594372	0.0509	-0.0522 -0.0195	-0.0717	-0.0209
1.00	0.7046678	0.0598	-0.0500 -0.0238	-0.0801	-0.0203
1.10	0.9299361	0.1025	-0.0433 -0.0791	-0.1224	-0.0198
1.20	1.1573688	0.1400	-0.0366 -0.1228	-0.1594	-0.0194
1.30	1.3919221	0.1697	-0.0321 -0.1535	-0.1856	-0.0159

Figure 3.1A THE CORRELATION ENERGY(He)

q =1.4068, MINIMUM Ec = −0.0226 a.u.

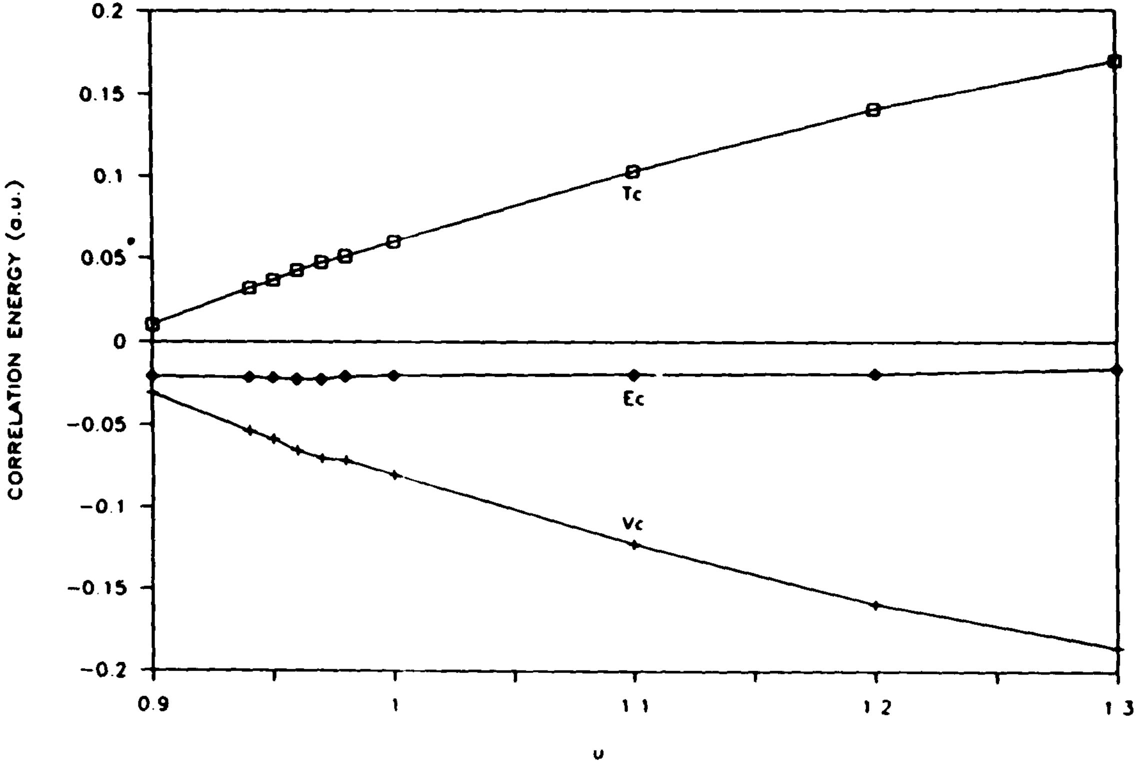


Figure 3.1B A CALCULATION FOR Ec OF He

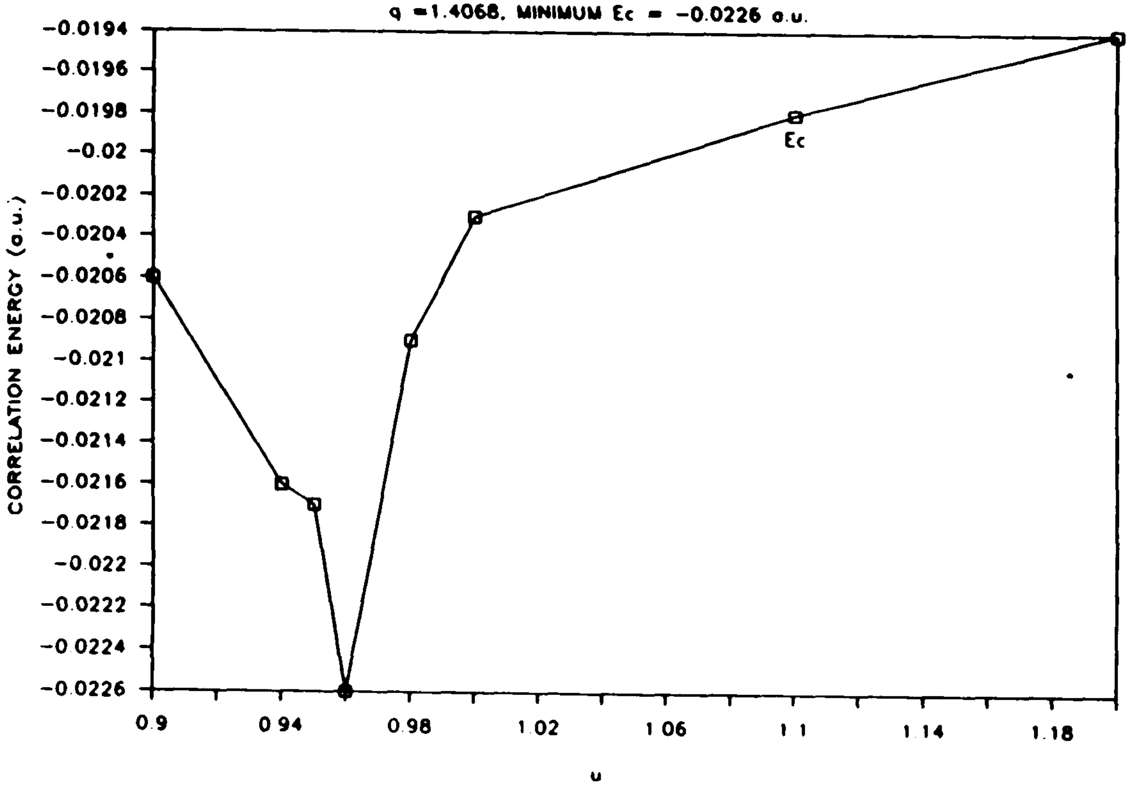


TABLE 4.1B THE CORRELATION ENERGY OF He ISOELECTRONIC ION Li^+ CALCULATED BY VARYING THE u PARAMETER

(q = 1.4068)

Li^+ u	t	Tc	Vc(1)/Vc(2)	Vc	Ec
0.94	0.5126082	0.0128	-0.0674 0.0359	-0.0315	-0.0188
0.96	0.5712420	0.0450	-0.0630 -0.0051	-0.0681	-0.0231
0.97	0.6030703	0.0577	-0.0618 -0.0176	-0.0794	-0.0217
1.00	0.6962351	0.0997	-0.0572 -0.0623	-0.1209	-0.0213
1.10	1.0119278	0.2200	-0.0449 -0.1861	-0.2352	-0.0152
1.20	1.3303915	0.3270	-0.0331 -0.3012	-0.3395	-0.0125
1.30	1.6576583	0.4151	-0.0227 -0.3972	-0.4199	-0.0

****

Figure 3.2A THE CORRELATION ENERGY(Li+)

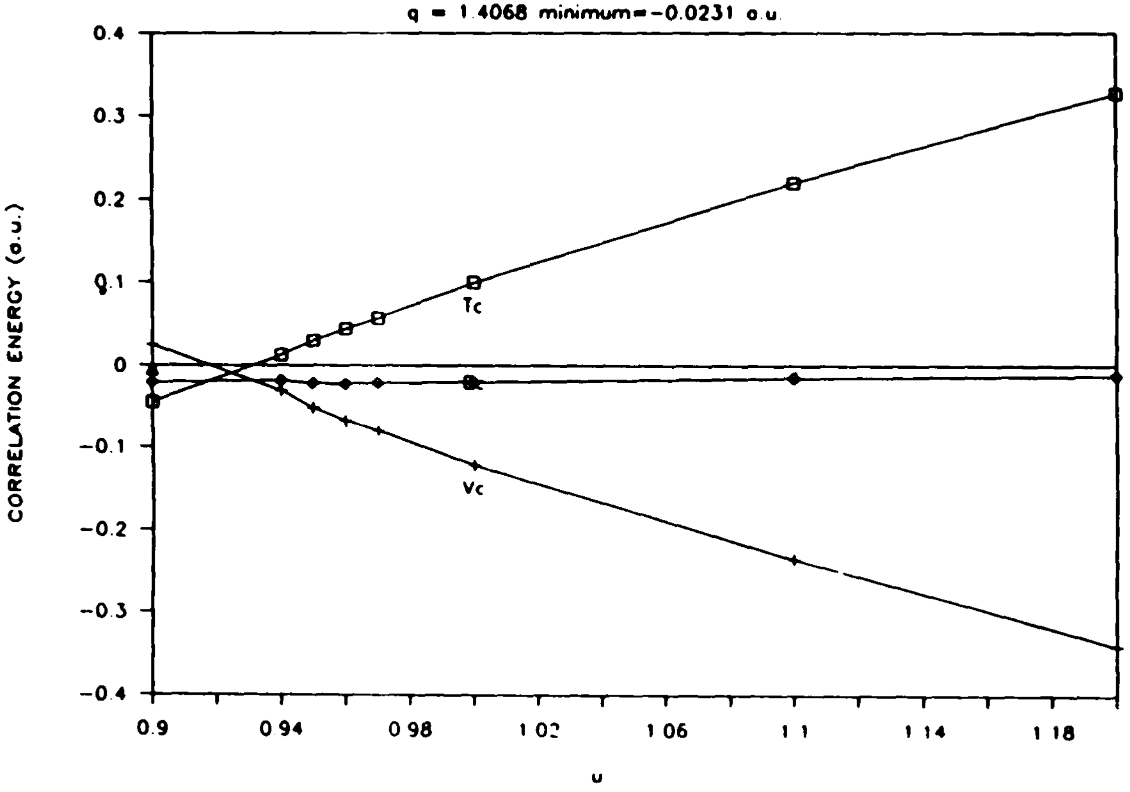


Figure 3.2B A CALCULATION FOR Ec OF Li+

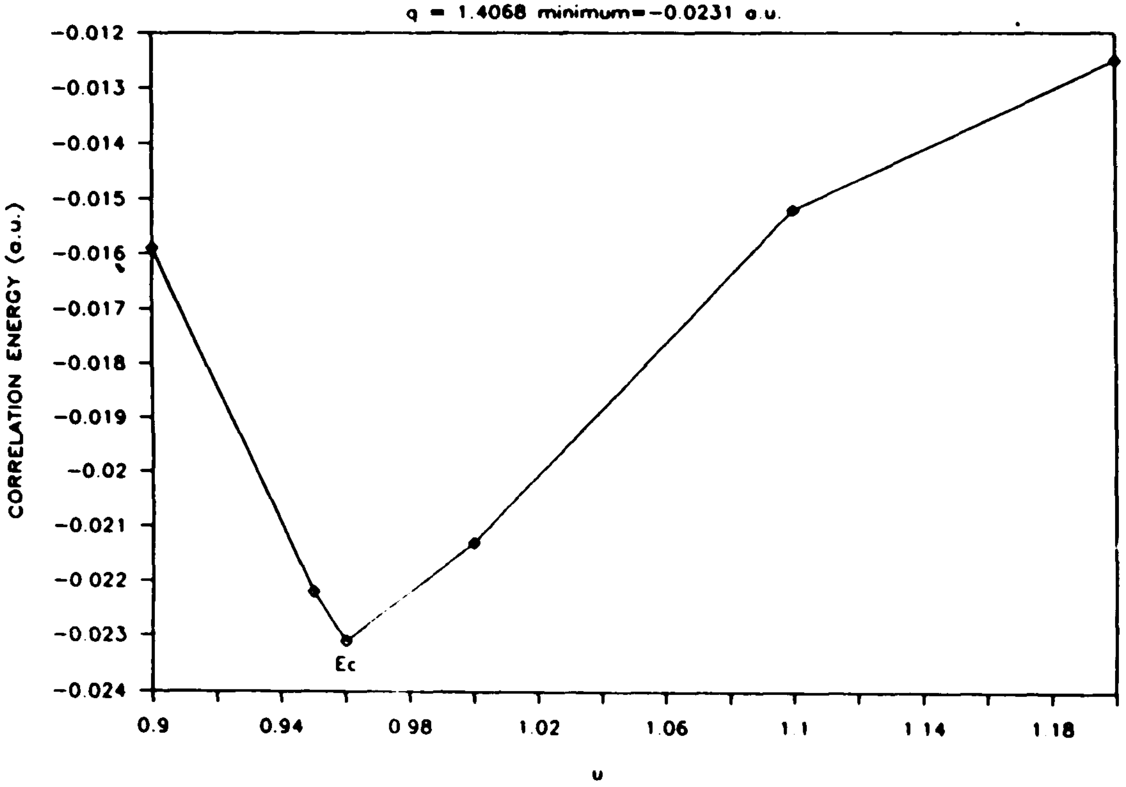


TABLE 4.1C THE CORRELATION ENERGY OF He ISOELECTRONIC ION Be^{+2} CALCULATED BY VARYING THE u PARAMETER

(q = 1.4068)

Be^{+2} u	t	Tc	Vc(1)/Vc(2)	Vc	Ec
0.96	0.5343898	0.0256	-0.0703 0.0230	-0.0472	-0.0216
0.97	0.5723571	0.0562	-0.0673 -0.0130	-0.0803	-0.0240
0.98	0.6125605	0.0826	-0.0653 -0.0392	-0.1045	-0.0219
1.00	0.6929689	0.1350	-0.0613 -0.0926	-0.1540	-0.0190
1.10	1.0985960	0.3757	-0.0420 -0.3427	-0.3847	-0.0090
1.20	1.5100455	0.5869	-0.0246 -0.5653	-0.5899	-0.0030

Figure 3.3A CORRELATION ENERGY Be(+2)

q = 1.4068 minimum=-0.0240 a.u.

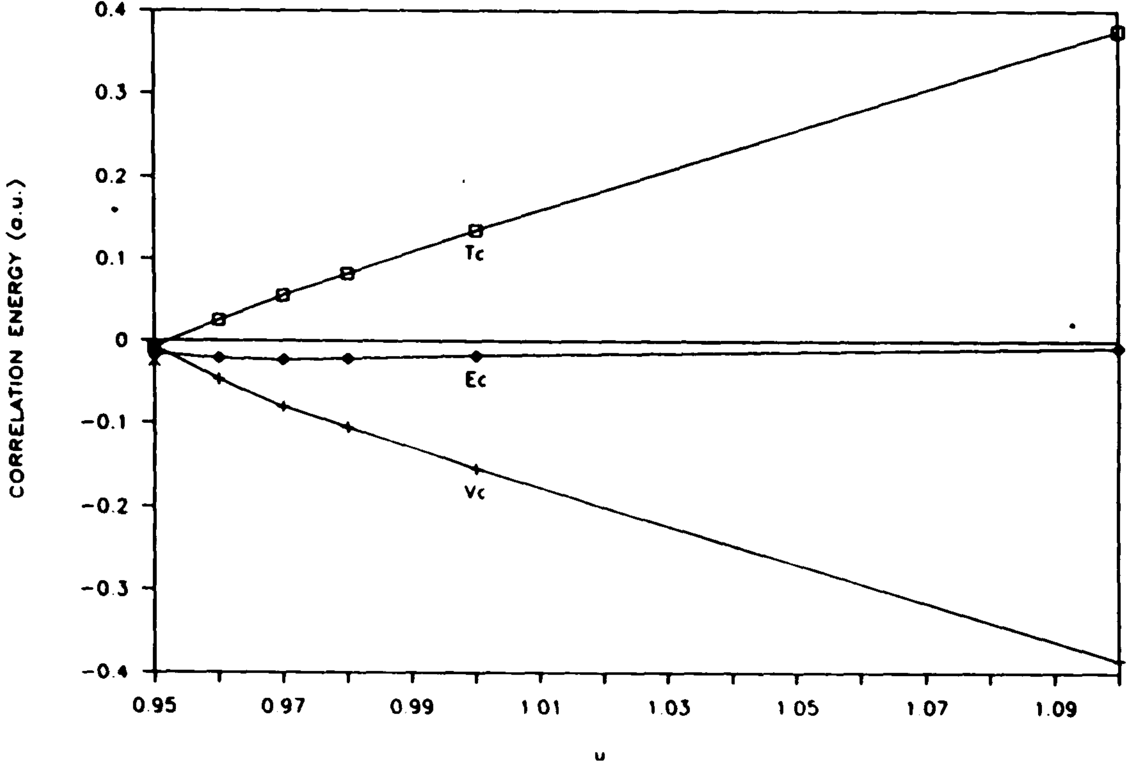


Figure 3.3B A CALCULATION FOR Ec Be(+2)

q = 1.4068 minimum=-0.0240 a.u.

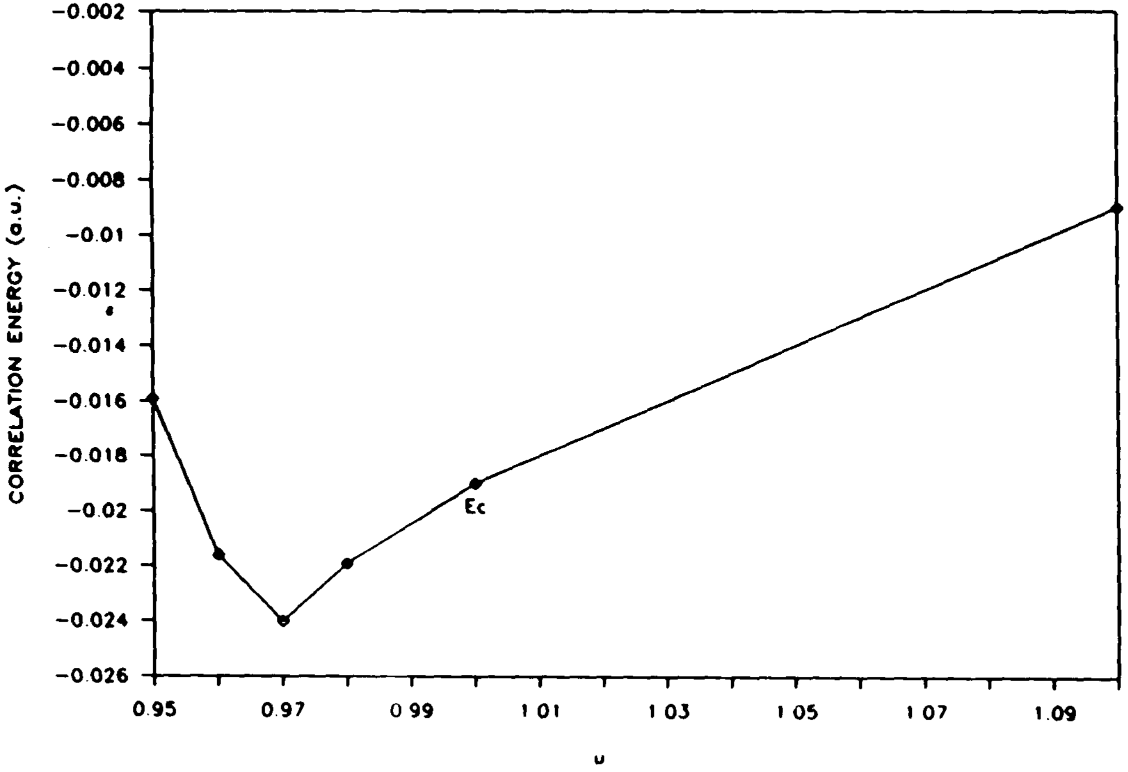


TABLE 4.1D THE CORRELATION ENERGY OF He ISOELECTRONIC ION B^{+3} CALCULATED BY VARYING THE u PARAMETER

($q = 1.4068$)

B^{+3} u	t	Tc	Vc(1)/Vc(2)	Vc	Ec
0.965	0.5224462	0.0082	-0.0750 0.0484	-0.0267	-0.0184
0.970	0.5454866	0.0341	-0.0730 0.0176	-0.0554	-0.0213
0.980	0.5942741	0.0796	-0.0702 -0.0278	-0.0980	-0.0183
1.000	0.6918364	0.1689	-0.0646 -0.1190	-0.1835	-0.0146
1.070	1.0332787	0.4707	-0.0443 -0.4401	-0.4844	-0.0136
1.100	1.1840386	0.5844	-0.0373 -0.5535	-0.5908	-0.0064

Figure 3.4A CORRELATION ENERGY OF B(+3)

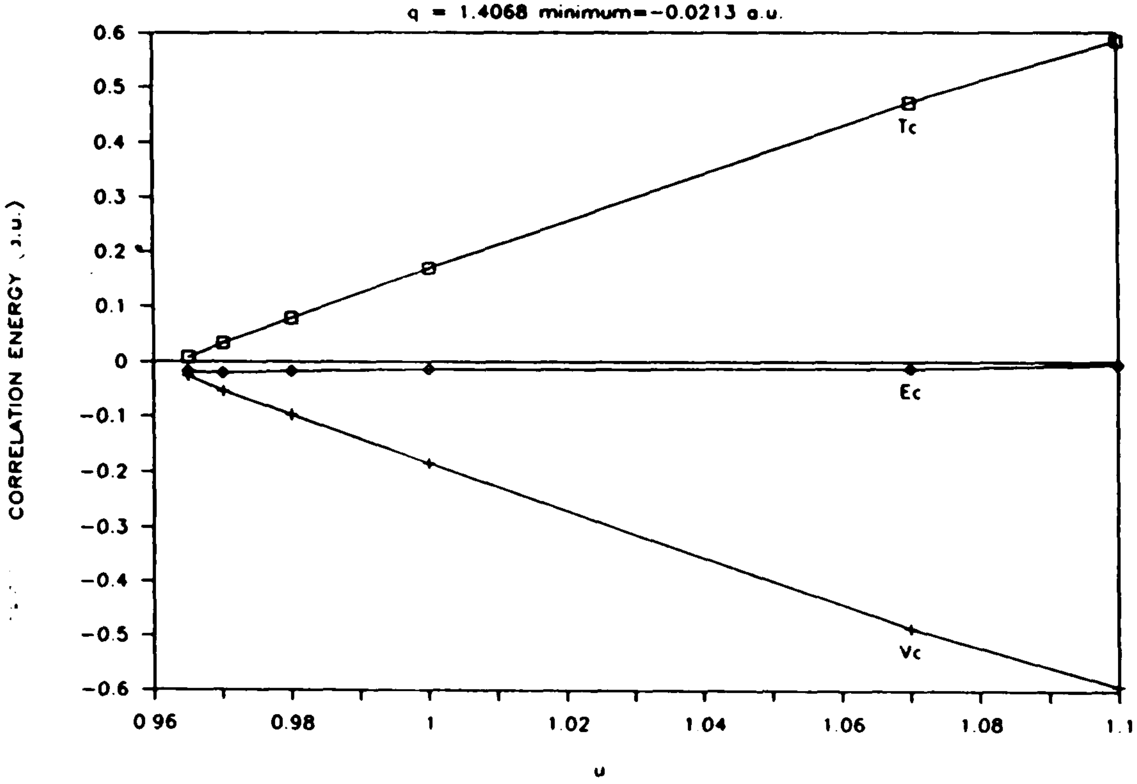


Figure 3.4B A CALCULATION FOR Ec/B(+3)

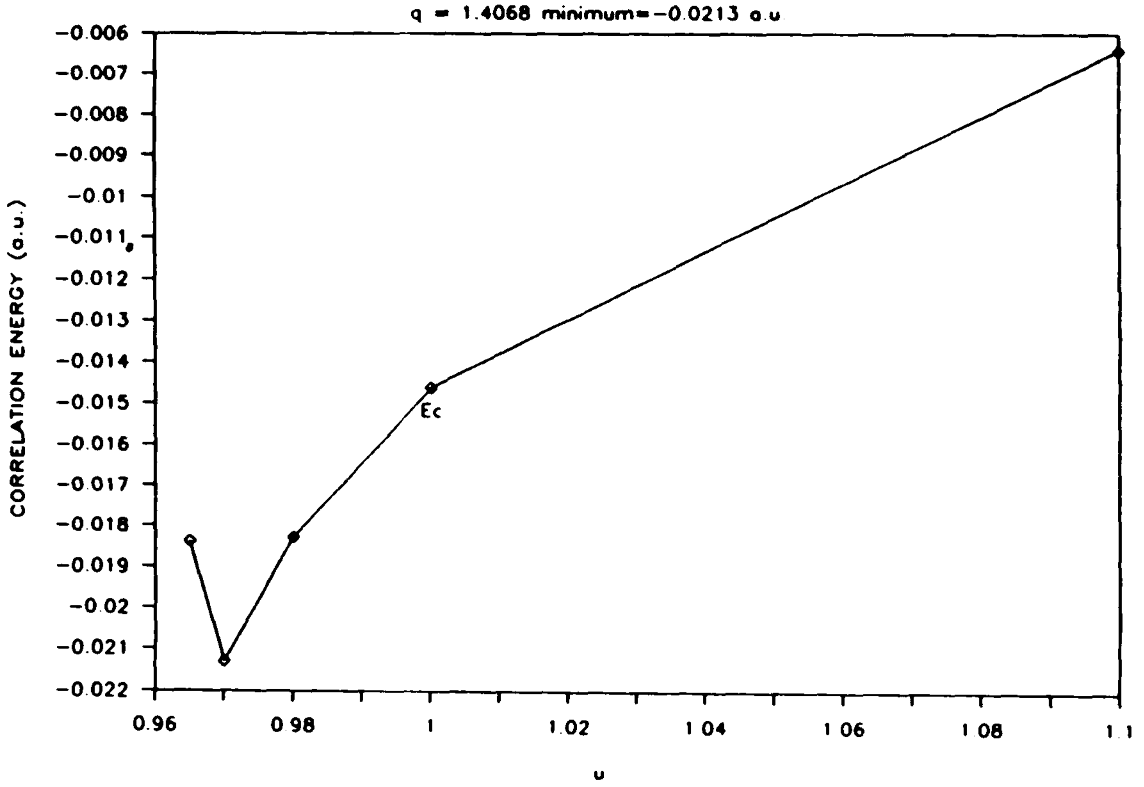


TABLE 4.2 THE LIST OF THE CORRELATION ENERGY OF He AND ITS ISOELECTRONIC IONS AT THE MINIMUM

(q = 1.4068)

	He	Li^{+}	Be^{+2}	B+3
u	0.96	0.96	0.97	0.97
t	0.612849	0.571242	0.572357	0.545487
Tc	0.0428	0.0450	0.0562	0.0341
Vc(1)	-0.0532	-0.0630	-0.0673	-0.0730
Vc(2)	-0.0121	-0.0051	-0.0130	0.0176
Vc	-0.0702	-0.0681	-0.0803	-0.0554
Ec	-0.0226	-0.0231	-0.0240	-0.0213
Ec (Clementi)	-0.0421	-0.0435	-0.0443	-0.0448
$\frac{\text{Ec(Cal.)}}{\text{Ec(Clementi)}}$	54 %	53%	54%	48%

Table 4.3A THE CALCULATION OF THE CORRELATION ENERGY OF He ATOM BY VARYING BOTH u AND q PARAMETERS

He u=1.00

q	t	Vc(1)/Vc(2)	Vc	Tc	Ec (Unit: a.u.)
0.70	0.46233469	-0.0996 0.0537	-0.0460	0.0210	-0.0250
0.77	0.49412486	-0.0928 0.0303	-0.0624	0.0354	-0.0271
0.80	0.50728059	-0.0901 0.0228	-0.0674	0.0401	-0.0272
0.81	0.51157230	-0.0893 0.0203	-0.0689	0.0416	-0.0273
0.90	0.54865986	-0.0821 0.0031	-0.0790	0.0521	-0.0268
1.00	0.58547395	-0.0743 -0.0133	-0.0871	0.0606	-0.0265
1.10	0.61992025	-0.0679 -0.0205	-0.0884	0.0635	-0.0249
1.20	0.64934248	-0.0612 -0.0291	-0.0903	0.0655	-0.0248

Table 4.3B THE CALCULATION OF THE CORRELATION ENERGY OF He ATOM BY VARYING BOTH u AND q PARAMETERS

He u=0.97

q	t	Vc(1)/Vc(2)	Vc	Tc	Ec (Unit: a.u.)
0.80	0.46397403	-0.0927 0.0417	-0.0511	0.0221	-0.0289
0.90	0.50049251	-0.0843 0.0196	-0.0647	0.0356	-0.0291
1.00	0.53317547	-0.0766 0.0033	-0.0732	0.0444	-0.0288
1.10	0.56190836	-0.0693 -0.0094	-0.0787	0.0500	-0.0286
1.20	0.58752078	-0.0628 -0.0174	-0.0802	0.0523	-0.0279
1.30	0.61046767	-0.0569 -0.0215	-0.0785	0.0520	-0.0265
u=0.95					
0.80	0.43602830	-0.0953 0.0596	-0.0357	0.0078	-0.0279
0.90	0.46951395	-0.0866 0.0358	-0.0508	0.0222	-0.0286
1.00	0.49902606	-0.0785 0.0172	-0.0613	0.0323	-0.0291
1.10	0.52507025	-0.0712 0.0038	-0.0674	0.0394	-0.0298
1.20	0.54634184	-0.0637 -0.0097	-0.0734	0.0432	-0.0301
1.30	0.56867921	-0.0587 -0.0094	-0.0681	0.0415	-0.0266
1.40	0.58696079	-0.0535 -0.0111	-0.0647	0.0399	-0.0248

Table 4.3C THE CALCULATION OF THE CORRELATION ENERGY OF He ATOM BY VARYING BOTH u AND q PARAMETERS

He u=0.93

q	t	Vc(1)/Vc(2)	Vc	Tc	Ec (Unit: a.u.)
0.90	0.43823978	-0.0887 0.0507	-0.0380	0.0091	-0.0289
1.00	0.46503213	-0.0805 0.0317	-0.0489	0.0197	-0.0292
1.10	0.48849687	-0.0732 0.0179	-0.0553	0.0263	-0.0289
1.20	0.50907588	-0.0665 0.0088	-0.0578	0.0298	-0.0280
1.30	0.52709681	-0.0606 0.0033	-0.0573	0.0307	-0.0266

Figure 4.1 Ec of He ATOM

From double parameters q and u

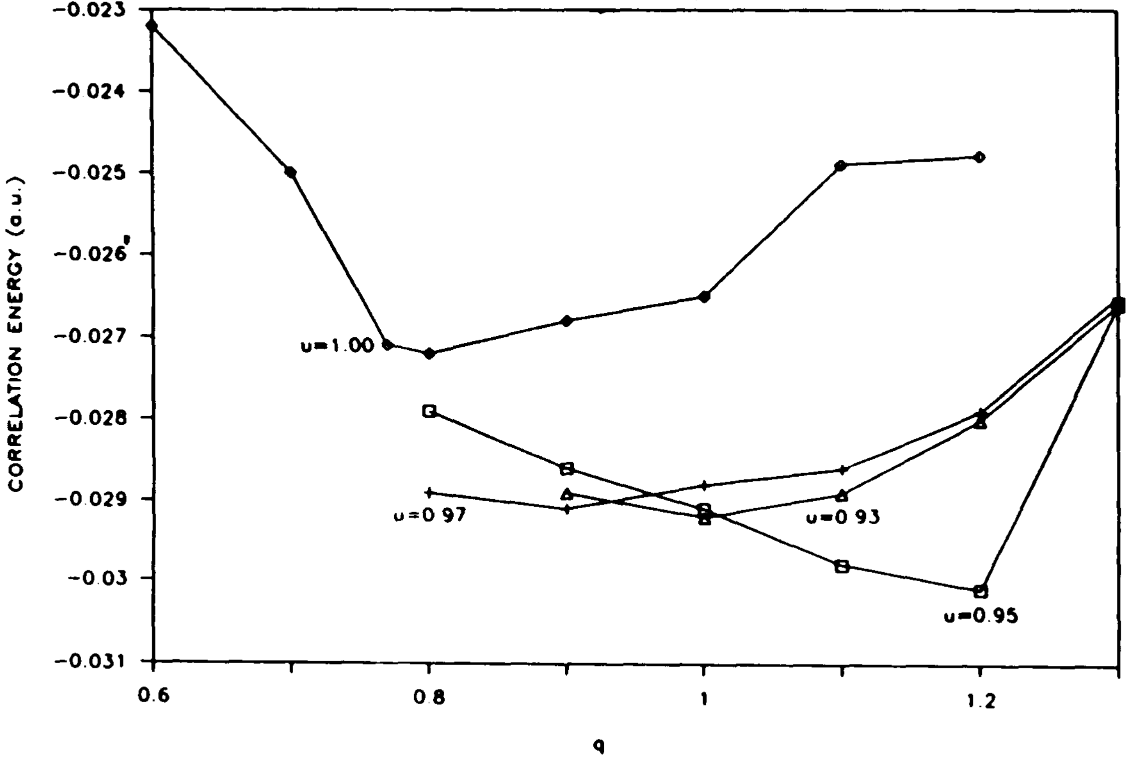


Table 4.4A THE CALCULATION OF THE CORRELATION ENERGY OF Li(+) ION BY VARYING BOTH u AND q PARAMETERS

Li^+ u=1.00 q	t	Vc(1)/Vc(2)	Vc	Tc	Ec (Unit: a.u.)
0.70	0.45761567	-0.1166 0.0683	-0.0483	0.0303	-0.0180
0.80	0.50229573	-0.1051 0.0187	-0.0864	0.0634	-0.0230
0.90	0.54215688	-0.0939 -0.0206	-0.1145	0.0903	-0.0242
1.00	0.57838076	-0.0845 -0.0469	-0.1315	0.1045	-0.0270
1.10	0.61089557	-0.0761 -0.0644	-0.1405	0.1119	-0.0286
1.20	0.64026922	-0.0685 -0.0737	-0.1422	0.1137	-0.0286
1.30	0.66679412	-0.0618 -0.0772	-0.1391	0.1109	-0.0281
1.41	0.6962351		-0.1209	0.0997	-0.0213

Table 4.4B THE CALCULATION OF THE CORRELATION ENERGY
OF Li(+) ION BY VARYING BOTH u AND q PARAMETERS

Li$^+$	u=0.96				
q	t	Vc(1)/Vc(2)	Vc	Tc	Ec (Unit: a.u.)
0.90	0.45776379	-0.1026 0.0704	-0.0322	0.0121	-0.0200
1.00	0.48526198	-0.0922 0.0327	-0.0595	0.0330	-0.0264
1.10	0.51157230	-0.0843 0.0185	-0.0658	0.0411	-0.0247

Table 4.4C THE CALCULATION OF THE CORRELATION ENERGY
OF Li(+) ION BY 3D SI

Li$^+$	u=1.10				
q	t	Vc(1)/Vc(2)	Vc	Tc	Ec (Unit: a.u.)
0.90	0.76062948	-0.0780 -0.1907	-0.2687	0.2511	-0.0176
1.00	0.81680536	-0.0690 -0.2107	-0.2797	0.2585	-0.0212
1.10	0.86864668	-0.0609 -0.2210	-0.2819	0.2584	-0.0235
1.20	0.91664743	-0.0538 -0.2238	-0.2776	0.2524	-0.0252
1.30	0.96132886	-0.0475 -0.2189	-0.2664	0.2419	-0.0245

Figure 4.2 Ec of Li(+) ION

From double parameters q and u

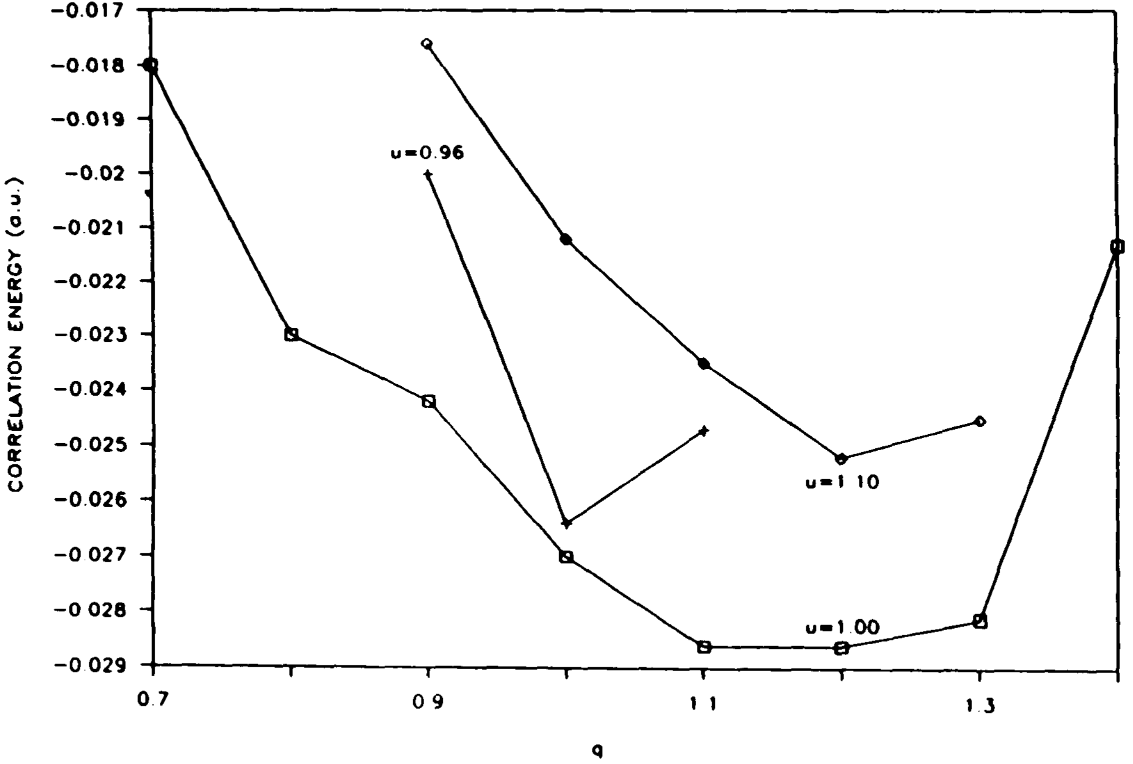


Table 4.5A THE CALCULATION OF THE CORRELATION ENERGY OF Be(+2) ION BY VARYING BOTH u AND q PARAMETERS

Be^{+}2 u=1.00

q	t	Vc(1)/Vc(2)	Vc	Tc	Ec (Unit: a.u.)
0.70	0.45399186	-0.1248 0.0701	-0.0547	0.0450	-0.0097
0.90	0.54025471	-0.1027 -0.0281	-0.1308	0.1159	-0.0149
1.00	0.57683742	-0.0926 -0.0611	-0.1537	0.1355	-0.0182
1.10	0.60705656	-0.0816 -0.1031	-0.1847	0.1545	-0.0303
1.20	0.63621616	-0.0734 -0.1143	-0.1878	0.1567	-0.0311
1.30	0.66295594	-0.0663 -0.1155	-0.1819	0.1518	-0.0301

* * *

Be^{+}2 u=0.97

q	t	Vc(1)/Vc(2)	Vc	Tc	Ec (Unit: a.u.)
1.00	0.48500440	-0.0988 0.0297	-0.0691	0.0390	-0.0301
1.10	0.50998199	-0.0893 0.0021	-0.0871	0.0550	-0.0322
1.20	0.53210580	-0.0809 -0.0141	-0.0949	0.0623	-0.0326
1.30	0.55151433	-0.0733 -0.0227	-0.0960	0.0641	-0.0319

* * *

Table 4.5B THE CALCULATION OF THE CORRELATION ENERGY OF Be(+2) ION BY VARYING BOTH u AND q PARAMETERS

$Be^{+}2$ q	u=0.96 t	Vc(1)/Vc(2)	Vc	Tc	Ec (Unit: a.u.)
1.00	0.45519423	-0.1015 0.0672	-0.0343	0.0033	-0.0310
1.10	0.47788617	-0.0920 0.0390	-0.0530	0.0206	-0.0323
1.20	0.49755937	-0.0834 0.0205	-0.0629	0.0304	-0.0325
1.30	0.51480752	-0.0758 0.0106	-0.0653	0.0334	-0.0319

Figure 4.3 Ec of Be(+2) ion

From double parameters q and u

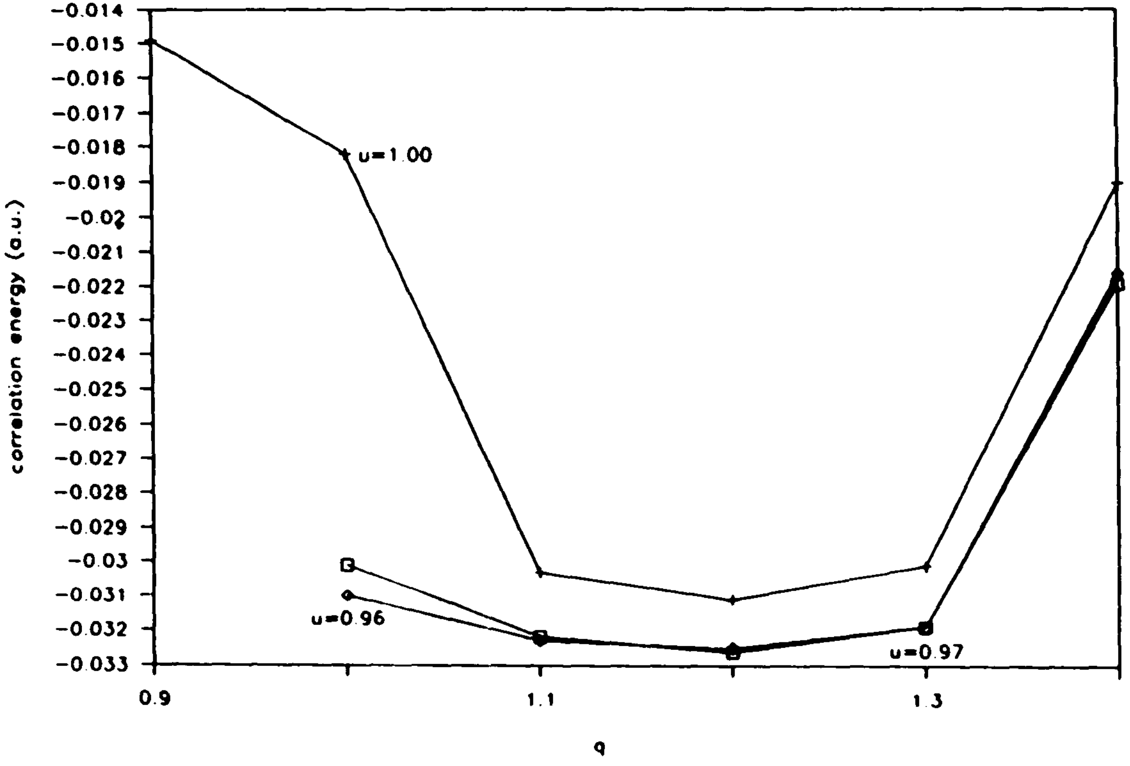


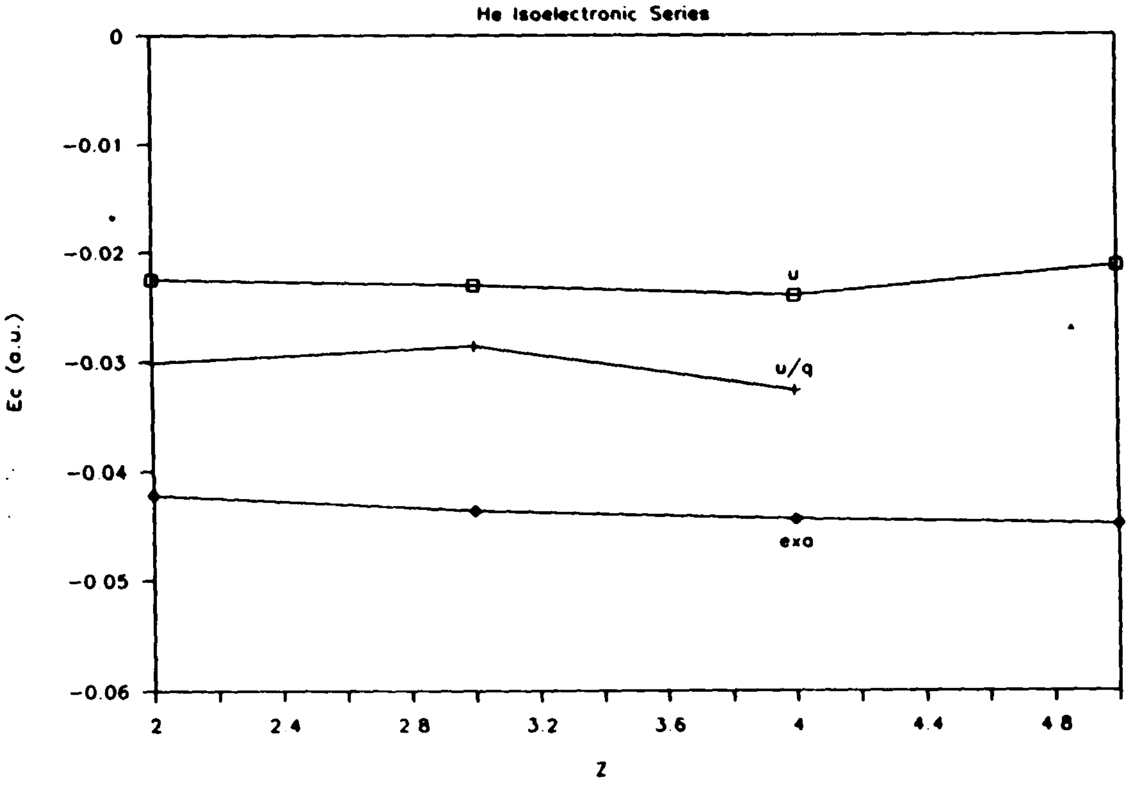
Table 4.6 THE BEST VALUES OF THE CORRELATION ENERGY OF He AND ITS ISOELECTRONIC IONS BY 3D SI WITH VARYING BOTH q AND u PARAMETERS

	He	Li^+	Be^{+2}
q	1.20	1.20	1.20
u	0.95	1.00	0.97
t	0.54634184	0.64026922	0.53210580
Tc	0.0432	0.1137	0.0623
Vc(1)	-0.0637	-0.0685	-0.0809
Vc(2)	-0.0097	-0.0737	-0.1143
Vc	-0.0734	-0.1422	-0.0949
Ec	-0.0301	-0.0286	-0.0326
Ec(Clementi)	-0.0421	-0.0435	-0.0443
$\frac{Ec(Cal.)}{Ec(Clementi)}$	73%	66%	74%

Table 4.7 THE CORRELATION ENERGY Ec OF He AND ITS ISOELECTRONIC IONS CALCULATED BY 3D SI AND COMPARED WITH THE NEARLY EXACT VALUES [3,4]

	He	Li^+	Be^{+2}	B+3
Ec(Clementi)	-0.0421	-0.0435	-0.0443	-0.0448
<u>One Variational Parameter u</u>				
u	0.96	0.96	0.97	0.97
t	0.612849	0.571242	0.572357	0.545487
Ec	-0.0226	-0.0231	-0.0240	-0.0213
$\frac{\text{Ec(Cal.)}}{\text{Ec(Clementi)}}$	54 %	53%	54%	48%
<u>Two Variational Parameters u and q</u>				
q	1.20	1.20	1.20	
u	0.95	1.00	0.96	
t	0.5463418	0.6402692	0.5321058	
Ec	-0.0301	-0.0286	-0.0326	
$\frac{\text{Ec(Cal.)}}{\text{Ec(Clementi)}}$	73%	66%	74%	

Figure 5.1 A COMPARISON OF Ec VALUES



(D) CONCLUSION

The correlation energies for He and some of its isoelectronic ions are found to be about 70% of the exact Ec. The correlation energy in this thesis is nonrelativistic regarding the usual Hamiltonian. It includes the potential and kinetic terms of the correlation energy. Our calculations give values from -0.031 to -0.033 a.u.. The exact Ec of He and its isoelectronic series fall within the range -0.042 to -0.047 a.u. [3,4].

We define the percentage correlation to be the percentage of the calculated correlation energy over the HF energy in percentage.

$$J = \frac{E_{cor}}{E_{HF}} \times 100\% \qquad (4\text{-}36)$$

where Ecor represents any term in the correlation energy, E_{HF} represents the terms of the HF energy, which is correlated by the Ecor. The percentage correlation for He atom is listed on Table 4.8.

Vc(1) is the most important contribution for Ec giving largest percentage correlation over -3%. The percentage correlation of other terms are 0.15% to 1.5%. This phenomenon reflects the fact [65] that Coulombic interaction between pairs of electrons, especially electrons with antiparallel spins as in the closed-shell case of the ground state of He isoelectronic series, is not properly accounted for by the HF method. The HF method just allows each electron to move in a "smeared-out" field of the others. Electrons of parallel spins are kept apart by the antisymmetry principle; the electrons with antiparallel spins avoid each other also. The HF method overrides the Coulombic repulsion by considering the electronic effect alone. So Vc(1) gives a negative value to correct this problem introduced by the HF method.

The contribution of Vc(2) is important to reach the exact Ec. However, the percentage correlation from Vc(2) is less than 0.2%. This reflects the fact that the HF method and its central potential field model is very effective to calculate the potential energy V(2) of electron-nuclear attraction.

When the calculations are improved by varying the double parameters q and u, the Table 4.8 shows that only the percentage correlation of double electron term Vc(1) significantly change form -3.2% to -3.8%. The percentage correlation from Tc remains constant. This means the above improvement is only effective in the potential correlation energy.

The results also show Tc is positive and total Vc is negative. This means the HF method calculated the kinetic energy and the total potential energy insufficiently [65]. From Virial theorem

$$T^{HF} = - \tfrac{1}{2} V^{HF} = -E^{HF} \qquad (4-37)$$

which is satisfied by HF method, if the one electron system was calculated by HF method, the T value should be lower than the exact kinetic energy, so that the total energy E could be higher than the exact total energy which is required by the Variational principle.

The percentage correlation from Tc stays at 1.5%. It is clear this is a reasonable J value for Tc.

When q = 1.4068, the minimum values of Ec for our trials are around u=0.97 (Table 4.2). This u value perhaps is helpful to find the minimum of Ec for the He isoelectronic series. Actually the minimum of Ec for B^{+3} was found by calculating Ec at u=0.97 first, then calculating three or more points to make sure.

When both q and u are varied, the minimum values of Ec from the calculations have reached about 70% at u≈0.97 and q=1.20 for our trials (Table 4.6). The point (u≈0.97 and q=1.20) also is helpful to find out the Ec of more trials in the He isoelectronic series. So this point (u≈0.97 and q=1.20) may be called a characteristic point of He isoelectronic series.

Further work could improve the calculations of Ec by varying q in smaller intervals and calculating Ec from more example from the He isoelectronic series, as well as from Be and Ne isoelectronic series.

TABLE 4.8 THE PERCENTAGE CORRELATION FOR He ATOM [66]

CALCULATED CORRELATION ENERGY	HF ENERGY (unit:a.u.)	PERCENTAGE CORRELATION %
By changing single parameter u		
Vc(1)= -0.0532	V(1)= 1.68728	-3.2%
Vc(2)= -0.0121	V(2)= -7.41064	0.16%
Tc= 0.0428	T = 2.86168	1.5%
Ec=-0.0226	E = -2.86168	0.8%
By changing double parameters q and u		
Vc(1)= -0.0637	V(1)= 1.68728	-3.8%
Vc(2)= -0.0097	V(2)= -7.41064	0.13%
Tc=0.0432	T = 2.86168	1.5%
Ec=-0.0301	E =-0.28168	1.1%

APPENDIX 1 NUMERICAL COORDINATES IN 3 DIMENSIONS AND SIMPSON NUMERICAL INTEGRATION

(1) COORDINATES

The system of He atom and its isoelectronic series has 2 1s electrons in the ground state. They would be characterized by 6 dimensions.

Graph a1-1 gives coordinates (1) for this system. In these coordinates our hf orbital and correlation function only contain 3 independent variables r_1, r_2 and θ', which is the angle between r_1 and r_2.

Graph A1-2 gives similar coordinates (2) for this system. In these coordinates our HF orbitals and correlation function only contains 3 independent variables R, r and θ, which is the angle between R and r.

The integrals for the system can be preformed only over the 3 dimensions above, other dimensions are not contained the density matrix or the correlation function, so that their contributions just give an over all multiplicative constant. All integration with 3 dimensions are performed by our 3D Simpson integration program.

Both sets coordinates (1) and (2) are used for convenient integration of various different functions.

In the above coordinates the following relationship holds:

$$\vec{r}_1 = \vec{i}x_1 + \vec{j}y_1 + \vec{k}z_1 \tag{A1-1}$$

where $\vec{i}, \vec{j}, \vec{k}$ are the unit vectors on the $\vec{X}$, $\vec{Y}$, $\vec{Z}$ axes of the coordinate system.

$$\vec{r}_2 = \vec{i}x_2 + \vec{j}y_2 + \vec{k}z_2 \tag{A1-2}$$

$$\vec{R} = \frac{1}{2} (\vec{r}_1 + \vec{r}_2) = \vec{i}X + \vec{j}Y + \vec{k}Z \tag{A1-3}$$

$$= \frac{\vec{i}}{2} (x_1 + x_2) + \frac{\vec{j}}{2} (y_1 + y_2) + \frac{\vec{k}}{2} (z_1 + z_2)$$

$$\vec{r} = \vec{r}_1 - \vec{r}_2 = \vec{i}x + \vec{j}y + \vec{k}z \tag{A1-4}$$

$$= \vec{i}(x_1 - x_2) + \vec{j}(y_1 - y_2) + \vec{k}(z_1 - z_2)$$

$$\vec{r}_1 = \vec{R} + \frac{\vec{r}}{2} \tag{A1-5}$$

$$\vec{r}_1 = \vec{i}(X + \frac{x}{2}) + \vec{j}(Y + \frac{y}{2}) + \vec{k}(Z + \frac{z}{2}) \tag{A1-6}$$

$$\vec{r}_2 = \vec{R} - \frac{\vec{r}}{2} \tag{A1-7}$$

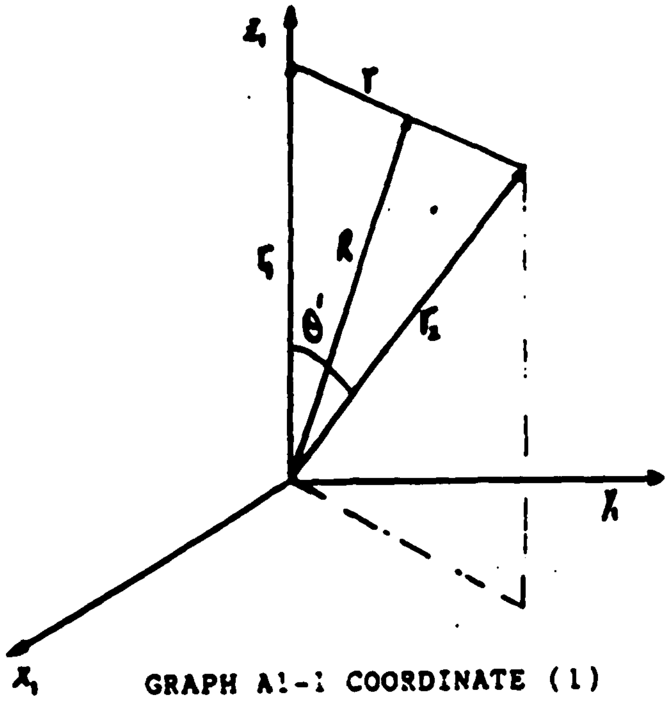
$$\vec{r}_2 = \vec{i}(X - \frac{x}{2}) + \vec{j}(Y - \frac{y}{2}) + \vec{k}(Z - \frac{z}{2}) \tag{A1-8}$$

$$R^2 = \frac{1}{4}\left(r_1^2 + r_2^2 + 2\, r_1 r_2 \cos\theta'\right) \tag{A1-9}$$

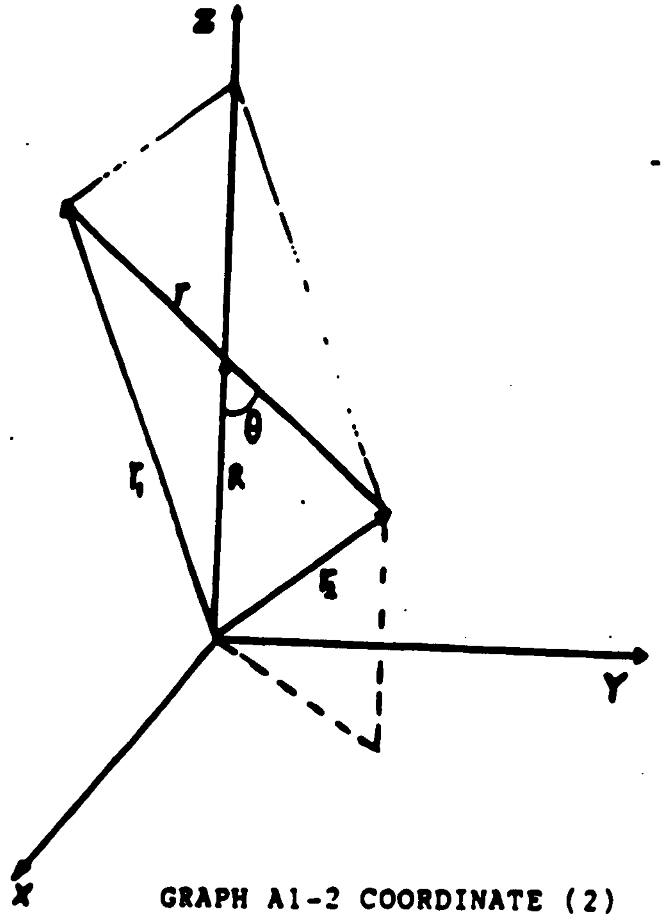
$$r^2 = r_1^2 + r_2^2 - 2\, r_1 r_2 \cos\theta' \tag{A1-10}$$

$$r_1^2 = R^2 + \frac{r^2}{4} + Rr\cos\theta \tag{A1-11}$$

$$r_2^2 = R^2 + \frac{r^2}{4} - Rr\cos\theta \tag{A1-12}$$



GRAPH A1-1 COORDINATE (1)



GRAPH A1-2 COORDINATE (2)

(2) 3 DIMENSIONAL SIMPSON NUMERICAL INTEGRATION

Simpson numerical integration with variable step size for one dimension is discussed in what follows

$$I = \int_a^b f(x)\ dx \tag{A1-13}$$

One may start with

$$T_1 = \frac{1}{2}\ [f(a) + f(b)] \cdot (b - a) \tag{A1-14}$$

Then the area may be separated according to following intervals

$$h_k = \frac{b - a}{2^k} \qquad k = 1,2,3,..... \tag{A1-15}$$

For each interval, half of the area is improved by the formula:

$$T_{2^k} = \frac{1}{2}\ T_{2^{k-1}} + h_k \cdot \sum_{i=1}^{2^{k-1}} f(x_i) \tag{A1-16}$$

where

$$x_i = a + h_i(2i-1) \tag{A1-17}$$

Finally the results of the integration could come from the summation

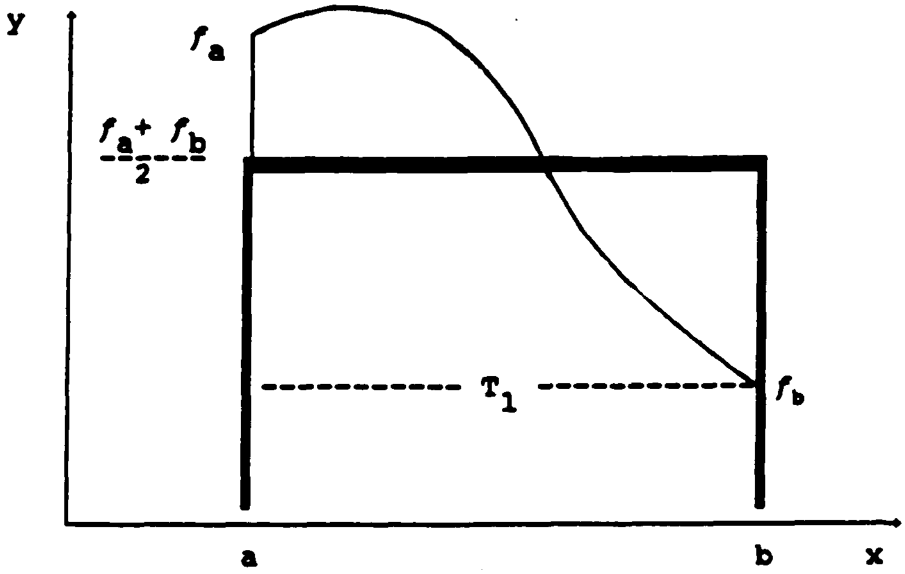
$$S_{2^k} = \frac{1}{3}\ (4T_{2^k} - T_{2^{k-1}}) \tag{A1-18}$$

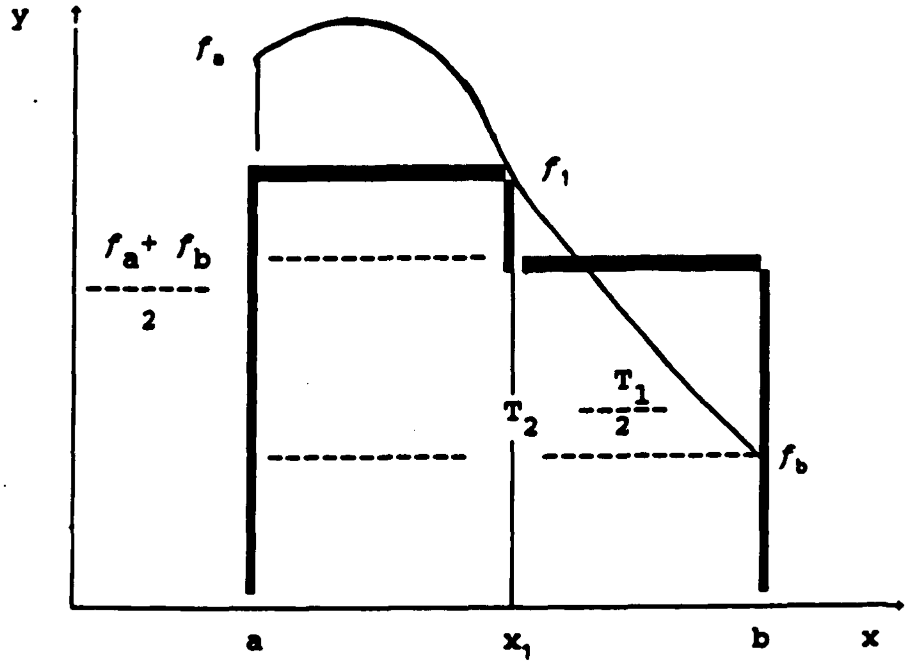
The calculation is stopped by a small enough value Epsilon ϵ being reached. When

$$|S_{2^k}-S_{2^{k-1}}| \le \epsilon\cdot(1+|S_{2^k}|) \qquad \text{(A1-19)}$$

the integration is completed.

The procedure is explained by the following graphs:





T_2 includes a half of T_1 and $f(x_1)\cdot\frac{1}{2}(b - a)$.

More points may be used to separate T_1 into more pieces, with 50% of the pieces improved by $f(x_i)$ each time. This is the basic idea of the Simpson method with variable steps.

Three dimensional integration by the Simpson method connect 3 single Simpson integrations. We have the integration

$$E = \int_0^{\pi} \sin\theta \, d\theta \int_0^{\infty} r^2 \, dr \int_0^{\infty} f(R, r, \underline{\cos\theta}) \, R^2 \, dR \qquad \text{(A1-20)}$$

The integration over θ may be transformed to integration over

$\cos\theta$, this is convenient for the integration of our function f, because our f only contains $\cos\theta$.

$$\int_0^{\pi} \sin\theta \, d\theta = \int_1^{-1} -d\underline{\cos\theta} = \int_{-1}^{1} d\underline{\cos\theta} \qquad \text{(A1-21)}$$

The integration over R is transformed also

$$\int_0^{\infty} f \; R^2 \; dR = \int_0^{1} f \; R^2 \; dR + \int_1^{\infty} f \; R^2 \; dR \qquad \text{(A1-22)}$$

Put

$$\tau = \frac{1}{R} \qquad \text{i.e.} \qquad R = \frac{1}{\tau} \qquad \text{(A1-23)}$$

$$d\,R = d\,\frac{1}{\tau} = \frac{-1}{\tau^2}\,d\tau \qquad \text{(A1-24)}$$

$$R^2 \; dR = \frac{-1}{\tau^4}\,d\tau \qquad \text{(A1-25)}$$

When R → 1, τ → 1; when R → ∞, τ → 0, so we have

$$\int_1^{\infty} f(R,r,\underline{\cos\theta}) \; R^2 \; dR = \int_1^{0} f(\tau,r,\underline{\cos\theta}) \; \frac{-1}{\tau^4}\,d\tau$$

$$= \int_0^{1} f(\tau,r,\underline{\cos\theta}) \; \frac{1}{\tau^4}\,d\tau \qquad \text{(A1-26)}$$

The entire integration over R could be performed as

$$\int_0^{\infty} f(R,r,\underline{\cos\theta}) \; R^2 \; dR = \qquad \text{(A1-27)}$$

$$\int_0^{1} f(R,r,\underline{\cos\theta}) \; R^2 \; dR + \int_0^{1} f(\tau,r,\underline{\cos\theta}) \; \frac{1}{\tau^4}\,d\tau$$

This formula is convenient for programming as it removes the infinity limit of integration. The integration over r is transformed in the same way. Suppose

$$\mu = \frac{1}{r} \qquad \text{i.e.} \qquad r = \frac{1}{\mu} \tag{A1-28}$$

$$d\,r = d\,\frac{1}{\mu} = \frac{-1}{\mu^2}\,d\mu \tag{A1-29}$$

$$\int_0^\infty f(R,r,\underline{\cos\theta})\ r^2\ dr = \tag{A1-30}$$

$$\int_0^1 f(R,r,\underline{\cos\theta})\ r^2\ dr + \int_0^1 f(\mu,r,\underline{\cos\theta})\ \frac{1}{\mu^4}\ d\mu$$

In the 3D Simpson integration, put a value $[\cos\theta]_1$ and a value of $[r]_1$ into the integration over R. When the integration over R under $[\cos\theta]_1$ and $[r]_1$ is completed, move $[r]_1$ to $[r]_2$ according to the Simpson procedure, and do the integration over R under the $[\cos\theta]_1$ and $[r]_2$ ..... Repeat this until the integration over r is completed, then move $[\cos\theta]_1$ to $[\cos\theta]_2$ according to the Simpson procedure, continue the integration until the integration over cosθ is completed. A computer program for the 3D Simpson integration has been written and applied in this thesis.

By the way, the other 3 dimensions (θ',ϕ,ϕ') which are independent of the function f, may be dealt with easily as follows

$$\int_0^\pi \sin\theta'\ d\theta' \int_0^{2\pi} d\phi' \int_0^{2\pi} d\phi = -\cos\theta' \Big|_0^\pi \cdot 2\pi \cdot 2\pi = 8\pi^2 \tag{A1-31}$$

APPENDIX (2) COLLE-SALVITTE NUMERICAL FORMULA

(1) THE NUMERICAL FORMULA

$$Ec = -0.04918 \int \frac{p(R)\ (1+0.173W*e^{\frac{-0.58}{\beta}}\ )}{1+\frac{0.8}{\beta}}\ d\vec{R} \qquad \text{(A2-1)}$$

where $d\vec{R}$ means a volume element: $R^2 dR \cdot \sin\theta d\theta \cdot d\phi$

$$W = 0.3814\ P^{-\frac{8}{3}}(R)\ [\nabla^2 P_2(1122)]_{r=0} \qquad \text{(A2-2)}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad \text{(A2-3)}$$

$$r^2 = x^2 + y^2 + z^2 = |\vec{r}_1 - \vec{r}_2|^2 \qquad \text{(A2-4)}$$

P_2 is the second order density matrix with spinless

$$P_2(1212) = p(11)p(22) - \frac{1}{2}\ p(12)p(21) \qquad \text{(A2-5)}$$

p is the first order density matrix.

(2). Hartree-Fock orbitals are taken from Clementi HF orbital table [57].

For He and its isoelectronic series

$p(11) = 2\ \Phi(1)\Phi(1)$ $\qquad$ $p(12) = 2\ \Phi(1)\Phi(2)$

$$p(21) = 2\ \Phi(2)\Phi(1) \qquad p(22) = 2\ \Phi(2)\Phi(2)$$

(A2-6)

where Φ is a HF 1S orbital function

$$\Phi(1) = \sum_{i=1}^{4} C_i(1s)*A_i(1s)*e^{-\alpha_i r_1} \qquad \text{(A)(A2-7)}$$

$$\Phi(2) = \sum_{i=1}^{4} C_i(1s)*A_i(1s)*e^{-\alpha_i r_2} \qquad \text{(B)(A2-7)}$$

$C_i(1s)$ are the coefficients of the 1s orbital, and the normalization constant $A_i(1s)$ is

$$A_i(1s) = \left(\frac{\alpha_i^3}{\pi}\right)^{\frac{1}{2}} \qquad \text{(A2-8)}$$

For Be and its isoelectronic series

$$p(11) = 2\ \mu(1)\mu(1) + 2\ \Omega(1)\Omega(1) \qquad \text{(A)(A2-9)}$$

$$p(12) = 2\ \mu(1)\mu(2) + 2\ \Omega(1)\Omega(2) = p(21) \qquad \text{(B)(A2-9)}$$

$$p(22) = 2\ \mu(2)\mu(2) + 2\ \Omega(2)\Omega(2) \qquad \text{(C)(A2-9)}$$

where μ represents HF 1s orbitals of the Be series, Ω represents HF 2s orbitals of the Be series

$$\mu(1) = \sum_{i=1}^{2} C_i(1s)*A_i(1s)\ *e^{-\alpha_i r_1} + r_1*\sum_{j=3}^{5} C_j(1s)*A_j(1s)\ *e^{-\alpha_j r_1}$$

(A)(A2-10)

$$\mu(2) = \sum_{i=1}^{2} C_i(1s) * A_i(1s) \ * e^{-\alpha_i r_2} + r_2 * \sum_{j=3}^{5} C_j(1s) * A_j(1s) \ * e^{-\alpha_j r_2}$$

(B)(A2-10)

$$\Omega(1) = \sum_{i=1}^{2} C_i(2s) * A_i(2s) \ * e^{-\alpha_i r_1} + r_1 * \sum_{j=3}^{5} C_j(2s) * A_j(2s) \ * e^{-\alpha_j r_1}$$

(A)(A2-11)

$$\Omega(2) = \sum_{i=1}^{2} C_i(2s) * A_i(2s) \ * e^{-\alpha_i r_2} + r_2 * \sum_{j=3}^{5} C_j(2s) * A_j(2s) \ * e^{-\alpha_j r2}$$

(B)(A2-11)

where

$$A_i(1s) = \left(\frac{\alpha_i^3}{\pi} \right)^{\frac{1}{2}} \qquad \text{(A)(A2-12)}$$

$$A_i(2s) = \left(\frac{\alpha_i^3}{\pi} \right)^{\frac{1}{2}} \qquad \text{(B)(A2-12)}$$

$$A_j(1s) = \left(\frac{\alpha_j^5}{3\pi} \right)^{\frac{1}{2}} \qquad \text{(A)(A2-13)}$$

$$A_j(2s) = \left(\frac{\alpha_j^5}{3\pi} \right)^{\frac{1}{2}} \qquad \text{(B)(A2-13)}$$

For Ne and its isoelectronic series

$$p(11) = 2\ \mu(1)\mu(1) + 2\ \Omega(1)\Omega(1)$$

$$+ 2\ \sigma_x(1)\sigma_x(1) + 2\ \sigma_y(1)\sigma_y(1) + 2\ \sigma_z(1)\sigma_z(1)$$

(A) (A2-14)

$$p(12) = 2\ \mu(1)\mu(2) + 2\ \Omega(1)\Omega(2)$$

$$+ 2\ \sigma_x(1)\sigma_x(2) + 2\ \sigma_y(1)\sigma_y(2) + 2\ \sigma_z(1)\sigma_z(2)$$

(B) (A2-14)

$$p(22) = 2\ \mu(2)\mu(2) + 2\ \Omega(2)\Omega(2)$$

$$+ 2\ \sigma_x(2)\sigma_x(2) + 2\ \sigma_y(2)\sigma_y(2) + 2\ \sigma_z(2)\sigma_z(2)$$

(C) (A2-14)

where μ and Ω have the same form but with different coefficients than in the Be series. $\sigma_x, \sigma_y, \sigma_z$ represent the 2p orbitals of HF. They are

$$\sigma_x(1) = X_1 * \sum_{k=1}^{4} C_k(2P) * A_k(2P) * e^{-\alpha_k r_1} \qquad \text{(A) (A2-15)}$$

$$\sigma_y(1) = Y_1 * \sum_{k=1}^{4} C_k(2P) * A_k(2P) * e^{-\alpha_k r_1} \qquad \text{(B) (A2-15)}$$

$$\sigma_z(1) = Z_1 * \sum_{k=1}^{4} C_k(2P) * A_k(2P) * e^{-\alpha_k r_1} \qquad \text{(C) (A2-15)}$$

$$\sigma_x(2) = X_2 * \sum_{k=1}^{4} C_k(2P) * A_k(2P) * e^{-\alpha_k r_2} \qquad \text{(A) (A2-16)}$$

$$\sigma_y(2) = Y_2 * \sum_{k=1}^{4} C_k(2P) * A_k(2P) * e^{-\alpha_k r_2} \qquad \text{(B) (A2-16)}$$

$$\sigma_z(2) = Z_2 * \sum_{k=1}^{4} C_k(2P) * A_k(2P) * e^{-\alpha_k r_2} \qquad \text{(C) (A2-16)}$$

where $C_k(2P)$ and α_k are the HF orbital coefficients [57]. And the normalization constant $A_k(2P)$ should be

$$A_k(2P) = \left(\frac{\alpha_k^5}{\pi} \right)^{1/2} \qquad \text{(A2-17)}$$

(3). DERIVATIVE

The second order derivative $\nabla^2 P_2(1212)$ are

$$\nabla^2 P_2(1212) = p(11)\cdot\nabla^2 p(22)+p(22)\cdot\nabla^2 p(11)+2\nabla p(11)\cdot\nabla p(22) - \tfrac{1}{2}\, p(12)\cdot\nabla^2 p(21) - \tfrac{1}{2}\, p(21)\cdot\nabla^2 p(12) - \nabla p(12)\cdot\nabla p(21) \qquad \text{(A2-18)}$$

The basic vector relations are

$$\vec{r}_1 = \left(\vec{R} + \frac{\vec{r}}{2} \right) \qquad \vec{r}_2 = \left(\vec{R} - \frac{\vec{r}}{2} \right) \qquad \text{(A)(A2-19)}$$

$$\vec{R} = \tfrac{1}{2} \left(\vec{r}_1 + \vec{r}_2 \right) = \vec{i}\, X + \vec{j}\, Y + \vec{k}\, Z \qquad \text{(B)(A2-19)}$$

$$\vec{r} = \vec{r}_1 - \vec{r}_2 = \vec{i}\cdot x + \vec{j}\cdot y + \vec{k}\cdot z \qquad \text{(C)(A2-19)}$$

where $\vec{i}$, $\vec{j}$, k are the unit vectors in the cartesian coordinate of Appendix 1. According to the above relationship we have

$$\vec{r}_1 = \vec{i}\,\left(X + \frac{x}{2}\right) + \vec{j}\,\left(Y + \frac{y}{2}\right) + \vec{k}\,\left(Z + \frac{z}{2}\right) \qquad \text{(A)(A2-20)}$$

$$\vec{r}_2 = \vec{i}\,(X - \frac{x}{2}) + \vec{j}\,(Y - \frac{y}{2}) + \vec{k}\,(Z - \frac{z}{2}) \qquad \text{(B)(A2-20)}$$

$$r_1^2 = x_1^2 + y_1^2 + z_1^2 \qquad \text{(A)(A2-21)}$$

$$= (X + \frac{x}{2})^2 + (Y + \frac{y}{2})^2 + (Z + \frac{z}{2})^2$$

$$r_2^2 = x_2^2 + y_2^2 + z_2^2 \qquad \text{(B)(A2-21)}$$

$$= (X - \frac{x}{2})^2 + (Y - \frac{y}{2})^2 + (Z - \frac{z}{2})^2$$

The derivative of basis functions are:

$$\nabla r = [\vec{i}\,\frac{\partial}{\partial x} + \vec{j}\,\frac{\partial}{\partial y} + \vec{k}\,\frac{\partial}{\partial z}]\,(x^2 + y^2 + z^2)^{\frac{1}{2}}$$

$$= \frac{\vec{r}}{r} \qquad \text{(A)(A2-22)}$$

$$\nabla r_1 = [\vec{i}\,\frac{\partial}{\partial x} + \vec{j}\,\frac{\partial}{\partial y} + \vec{k}\,\frac{\partial}{\partial z}]((X + \frac{x}{2})^2 + (Y + \frac{y}{2})^2 + (Z + \frac{z}{2})^2)^{\frac{1}{2}}$$

$$= \frac{\vec{r}_1}{2r_1} \qquad \text{(B)(A2-22)}$$

$$\nabla r_2 = [\vec{i}\,\frac{\partial}{\partial x} + \vec{j}\,\frac{\partial}{\partial y} + \vec{k}\,\frac{\partial}{\partial z}]((X - \frac{x}{2})^2 + (Y - \frac{y}{2})^2 + (Z - \frac{z}{2})^2)^{\frac{1}{2}}$$

$$= \frac{-\vec{r}_2}{2r_2} \qquad \text{(C)(A2-22)}$$

The second order derivatives are

$$\nabla^2 r = \nabla \frac{\vec{r}}{r} = \frac{2}{r} \qquad \text{(A)(A2-23)}$$

$$\nabla^2 r_1 = \nabla \frac{\vec{r}_1}{2r_1} = \frac{1}{2r_1} \qquad \text{(B)(A2-23)}$$

$$\nabla^2 r_2 = \nabla \frac{-\vec{r}_2}{2r_2} = \frac{1}{2r_2} \qquad \text{(C)(A2-23)}$$

(A) For He isoelectronic series ($1s^2$):
The first order derivatives are

$$\nabla p(11) = 4\ \Phi(1) \cdot \nabla\Phi(1) \qquad \text{(A)(A2-24)}$$

$$\nabla p(22) = 4\ \Phi(2) \cdot \nabla\Phi(2) \qquad \text{(B)(A2-24)}$$

$$\nabla p(12) = 2\ \Phi(1) \cdot \nabla\Phi(2) + 2\ \Phi(2) \cdot \nabla\Phi(1) \qquad \text{(C)(A2-24)}$$

$$\nabla\Phi(1) = \frac{\vec{r}_1}{2r_1} \sum_{i=1}^{4} C_i(1s)*A_i(1s)*(-\alpha_i)*e^{-\alpha_i r_1}$$

$$= \frac{\vec{r}_1}{2r_1} \bar{B}_1(1s) \qquad \text{(A2-25)}$$

where

$$\bar{B}_1(1s) = \sum_{i=1}^{4} C_i(1s)*A_i(1s)*(-\alpha_i)*e^{-\alpha_i r_1} \qquad \text{(A2-26)}$$

$$\nabla\Phi(2) = \frac{-\vec{r}_2}{2r_2} \sum_{i=1}^{4} C_i(1s)*A_i(1s)*(-\alpha_i)*e^{-\alpha_i r_2}$$

$$= \frac{-\vec{r}_2}{2r_2} \bar{B}_2(1s) \qquad \text{(A2-27)}$$

where

$$\bar{B}_2(1s) = \sum_{i=1}^{4} C_i(1s)*A_i(1s)*(-\alpha_i)*e^{-\alpha_i r_2} \qquad \text{(A2-28)}$$

$$\nabla\Phi(1)\cdot\nabla\Phi(1) = \frac{1}{4} [\bar{B}_1(1s)]^2 \qquad \text{(A)(A2-29)}$$

$$\nabla\Phi(2)\cdot\nabla\Phi(2) = \frac{1}{4} [\bar{B}_2(1s)]^2 \qquad \text{(B)(A2-29)}$$

$$\nabla\Phi(1)\cdot\nabla\Phi(2) = -\frac{1}{4} \frac{\vec{r}_1}{r_1}\frac{\vec{r}_2}{r_2} \bar{B}_1(1s)\cdot\bar{B}_2(1s) \qquad \text{(C)(A2-29)}$$

Second order derivatives

$$\nabla^2 p(11) = \nabla \{4\ \Phi(1)\ \nabla\Phi(1)\}$$

$$= 4\ \Phi(1)\ \nabla^2\Phi(1) + 4\ \nabla\Phi(1)\ \nabla\Phi(1) \qquad \text{(A)(A2-30)}$$

$$\nabla^2 p(22) = \nabla \{4\ \Phi(2)\ \nabla\Phi(2)\}$$

$$= 4\ \Phi(2)\ \nabla^2\Phi(2) + 4\ \nabla\Phi(2)\ \nabla\Phi(2) \qquad \text{(B)(A2-30)}$$

$$\nabla^2 p(12) = \nabla\{\ 2\Phi(1)\ \nabla\Phi(2) + 2\Phi(2)\ \nabla\Phi(1)\ \}$$

$$= 2\Phi(1)\ \nabla^2\Phi(2) + 2\Phi(2)\ \nabla^2\Phi(1) + 4\ \nabla\Phi(1)\ \nabla\Phi(2)$$

$$= \nabla^2 p(21) \qquad \text{(A2-31)}$$

$$\nabla^{2}\phi(1) = \nabla\left(\frac{\vec{r}_1}{2r_1} \bar{B}_1(1s) \right)$$

$$= \bar{B}_1(1s) \; \nabla \frac{\vec{r}_1}{2r_1} + \frac{\vec{r}_1}{2r_1} \nabla\bar{B}_1(1s)$$

$$= \frac{1}{2r_1} \bar{B}_1(1s) + \frac{1}{4} \tilde{B}_1(1s) \qquad \text{(A2-32)}$$

where

$$\tilde{B}_1(1s) = \sum_{i=1}^{4} C_i(1s) * A_i(1s) * (-\alpha_i)^{2} * e^{-\alpha_i r_1} \qquad \text{(A2-33)}$$

$$\nabla^{2}\phi(2) = \nabla\left(\frac{-\vec{r}_2}{2r_2} \bar{B}_2(1s) \right)$$

$$= \bar{B}_2(1s) \; \nabla \frac{-\vec{r}_2}{2r_2} + \frac{-\vec{r}_2}{2r_2} \nabla\bar{B}_2(1s)$$

$$= \frac{1}{2r_2} \bar{B}_2(1s) + \frac{1}{4} \tilde{B}_2(1s) \qquad \text{(A2-34)}$$

where

$$\tilde{B}_2(1s) = \sum_{i=1}^{4} C_i(1s) * A_i(1s) * (-\alpha_i)^{2} * e^{-\alpha_i r_2} \qquad \text{(A2-35)}$$

(B) For Be isoelectronic series ($1s^{2}2s^{2}$):
First order derivatives are:

$$\nabla p(11) = 4\,\mu(1)\,\nabla\mu(1) + 4\,\Omega(1)\,\nabla\Omega(1) \qquad \text{(A)(A2-36)}$$

$$\nabla p(22) = 4\ \mu(2)\ \nabla\mu(2) + 4\ \Omega(2)\ \nabla\Omega(2) \qquad \text{(B)(A2-36)}$$

$$\nabla p(12) = 2\ \mu(1)\ \nabla\mu(2) + 2\ \mu(2)\ \nabla\mu(1)$$
$$+ 2\ \Omega(1)\ \nabla\Omega(2) + 2\ \Omega(2)\ \nabla\Omega(1) \qquad \text{(C)(A2-36)}$$

$$\nabla\mu(1) = \frac{\vec{r}_1}{2r_1} \left(\bar{B}_1(1s) + D_1(1s) + r_1 * \bar{D}_1(1s) \right) \qquad \text{(A2-37)}$$

where

$$\bar{B}_1(1s) = \sum_{i=1}^{2} C_i(1s) * A_i(1s) * (-\alpha_i) * e^{-\alpha_i r_1} \qquad \text{(A2-38)}$$

$$D_1(1s) = \sum_{j=3}^{5} C_j(1s) * A_j(1s) * e^{-\alpha_j r_1} \qquad \text{(A2-39)}$$

$$\bar{D}_1(1s) = \sum_{j=3}^{5} C_j(1s) * A_j(1s) * (-\alpha_j) * e^{-\alpha_j r_1} \qquad \text{(A2-40)}$$

$$\nabla\mu(2) = -\frac{-\vec{r}_2}{2r_2} \left(\bar{B}_2(1s) + D_2(1s) + r_2 * \bar{D}_2(1s) \right) \qquad \text{(A2-41)}$$

where

$$\bar{B}_2(1s) = \sum_{i=1}^{2} C_i(1s) * A_i(1s) * (-\alpha_i) * e^{-\alpha_i r_2} \qquad \text{(A2-42)}$$

$$D_2(1s) = \sum_{j=3}^{5} C_j(1s) * A_j(1s) * e^{-\alpha_j r_2} \qquad \text{(A2-43)}$$

$$\bar{D}_2(1s) = \sum_{j=3}^{5} C_j(1s) * A_j(1s) * (-\alpha_j) * e^{-\alpha_j r_2} \qquad \text{(A2-44)}$$

$$\nabla\Omega(1) = \frac{\vec{r}_1}{2r_1} \left(\bar{B}_1(2s) + D_1(2s) + r_1 * \bar{D}_1(2s) \right) \qquad \text{(A2-45)}$$

where

$$\bar{B}_1(2s) = \sum_{i=1}^{2} C_i(2s) * A_i(2s) * (-\alpha_i) \; * e^{-\alpha_i r_1} \qquad \text{(A2-46)}$$

$$D_1(2s) = \sum_{j=3}^{5} C_j(2s) * A_j(2s) \; * e^{-\alpha_j r_1} \qquad \text{(A2-47)}$$

$$\bar{D}_1(2s) = \sum_{j=3}^{5} C_j(2s) * A_j(2s) * (-\alpha_j) \; * e^{-\alpha_j r_1} \qquad \text{(A2-48)}$$

$$\nabla\Omega(2) = \frac{-\vec{r}_2}{2r_2} \left(\bar{B}_2(2s) + D_2(2s) + r_2 * \bar{D}_2(2s) \right) \qquad \text{(A2-49)}$$

where

$$\bar{B}_2(2s) = \sum_{i=1}^{2} C_i(2s) * A_i(2s) * (-\alpha_i) \; * e^{-\alpha_i r_2} \qquad \text{(A2-50)}$$

$$D_2(2s) = \sum_{j=3}^{5} C_j(2s) * A_j(2s) \; * e^{-\alpha_j r_2} \qquad \text{(A2-51)}$$

$$\bar{D}_2(2s) = \sum_{j=3}^{5} C_j(2s) * A_j(2s) * (-\alpha_j) \; * e^{-\alpha_j r_2} \qquad \text{(A2-52)}$$

The second order derivatives for the Be series are

$$\begin{aligned} \nabla^2 \rho(11) &= \nabla \left(4\,\mu(1)\,\nabla\mu(1) + 4\,\Omega(1)\,\nabla\Omega(1) \right) \\ &= 4\,\mu(1)\,\nabla^2\mu(1) + 4\,\nabla\mu(1)\,\nabla\mu(1) \\ &\quad + 4\,\Omega(1)\,\nabla^2\Omega(1) + 4\,\nabla\Omega(1)\,\nabla\Omega(1) \qquad \text{(A)(A2-53)} \end{aligned}$$

$$\nabla^2 p(22) = \nabla \,(\; 4\; \mu(2)\; \nabla\mu(2) + 4\; \Omega(2)\; \nabla\Omega(2) \;)$$

$$= 4\; \mu(2)\; \nabla^2\mu(2) + 4\; \nabla\mu(2)\; \nabla\mu(2)$$

$$+ 4\; \Omega(2)\; \nabla^2\Omega(2) + 4\; \nabla\Omega(2)\; \nabla\Omega(2) \qquad \text{(B)(A2-53)}$$

$$\nabla^2 p(12) = \nabla(\; 2\mu(1)\; \nabla\mu(2) + 2\mu(2)\; \nabla\mu(1)$$

$$+ 2\Omega(1)\; \nabla\Omega(2) + 2\Omega(1)\; \nabla\Omega(2) \;)$$

$$= 2\mu(1)\; \nabla^2\mu(2) + 2\mu(2)\; \nabla^2\mu(1) + 4\; \nabla\mu(1)\; \nabla\mu(2)$$

$$+ 2\Omega(1)\; \nabla^2\Omega(2) + 2\Omega(2)\; \nabla^2\Omega(1) + 4\; \nabla\Omega(1)\; \nabla\Omega(2)$$

(A2-54)

$$\nabla^2 p(12) = \nabla^2 p(21) \qquad \text{(A2-55)}$$

$$\nabla^2\mu(1) = \nabla \,(\; \frac{\vec{r}_1}{2r_1} \,[\; \bar{B}_1(1s) + D_1(1s) + r_1 * \bar{D}_1(1s)] \;)$$

$$= \frac{2}{r_1} \,[\; \bar{B}_1(1s) + D_1(1s) + r_1 * \bar{D}_1(1s)]$$

$$+ \frac{1}{4} \,[\; \overset{-}{B}_1(1s) + 2\bar{D}_1(1s) + r_1 * \overset{-}{D}_1(1s) \;] \qquad \text{(A2-56)}$$

where

$$\overset{-}{B}_1(1s) = \sum_{i=1}^{2} C_i(1s) * A_i(1s) * (-\alpha_i)^2 \;\; * e^{-\alpha_i r_1} \qquad \text{(A2-57)}$$

$$\overset{-}{D}_1(1s) = \sum_{j=3}^{5} C_j(1s) * A_j(1s) * (-\alpha_j)^2 \;\; * e^{-\alpha_j r_1} \qquad \text{(A2-58)}$$

$$\nabla^2\mu(2) = \nabla\left(\frac{-\vec{r}_2}{2r_2} \left[\bar{B}_2(1s) + D_2(1s) + r_2 * \bar{D}_2(1s)\right] \right)$$

$$= -\frac{2}{r_2} \left[\bar{B}_2(1s) + D_2(1s) + r_2 * \bar{D}_2(1s)\right]$$

$$+ -\frac{1}{4} \left[\overset{-}{B}_2(1s) + 2\bar{D}_2(1s) + r_2 * \overset{-}{D}_2(1s) \right] \tag{A2-59}$$

where

$$\overset{-}{B}_2(1s) = \sum_{i=1}^{2} C_i(1s) * A_i(1s) * (-\alpha_i)^2 \ * e^{-\alpha_i r_2} \tag{A2-60}$$

$$\overset{-}{D}_2(1s) = \sum_{j=3}^{5} C_j(1s) * A_j(1s) * (-\alpha_j)^2 \ * e^{-\alpha_j r_2} \tag{A2-61}$$

$$\nabla^2\Omega(1) = \nabla\left(\frac{\vec{r}_1}{2r_1} \left[\bar{B}_1(2s) + D_1(2s) + r_1 * \bar{D}_1(2s)\right] \right)$$

$$= -\frac{2}{r_1} \left[\bar{B}_1(2s) + D_1(2s) + r_1 * \bar{D}_1(2s)\right]$$

$$+ -\frac{1}{4} \left[\overset{-}{B}_1(2s) + 2\bar{D}_1(2s) + r_1 * \overset{-}{D}_1(2s) \right] \tag{A2-62}$$

where

$$\overset{-}{B}_1(2s) = \sum_{i=1}^{2} C_i(2s) * A_i(2s) * (-\alpha_i)^2 \ * e^{-\alpha_i r_1} \tag{A2-63}$$

$$\overset{-}{D}_1(2s) = \sum_{j=3}^{5} C_j(2s) * A_j(2s) * (-\alpha_j)^2 \ * e^{-\alpha_j r_1} \tag{A2-64}$$

$$\nabla^2\Omega(2) = \nabla \left(\frac{-\vec{r}_2}{2r_2^2} [\bar{B}_2(2s) + D_2(2s) + r_2*\bar{D}_2(2s)] \right)$$

$$= -\frac{2}{r_2} [\bar{B}_2(2s) + D_2(2s) + r_2*\bar{D}_2(2s)]$$

$$+ -\frac{1}{4}- [\tilde{B}_2(2s) + 2\bar{D}_2(2s) + r_2*\tilde{D}_2(2s)]$$

(A2-65)

where

$$\tilde{B}_2(2s) = \sum_{i=1}^{2} C_i(2s)*A_i(2s)*(-\alpha_i)^2 \; *e^{-\alpha_i r_2} \qquad \text{(A2-66)}$$

$$\tilde{D}_2(2s) = \sum_{j=3}^{5} C_j(2s)*A_j(2s)*(-\alpha_j)^2 \; *e^{-\alpha_j r_2} \qquad \text{(A2-67)}$$

(C) For the Ne series ($1s^2 2s^2 2p^6$)

The first order derivatives of the Ne series are:

$$\nabla p(11) = 4\ \mu(1)\ \nabla\mu(1) + 4\ \Omega(1)\ \nabla\Omega(1) \qquad \text{(A)(A2-68)}$$

$$+ 4\ \sigma_x(1)\ \nabla\sigma_x(1) + 4\ \sigma_y(1)\ \nabla\sigma_y(1) + 4\ \sigma_z(1)\ \nabla\sigma_z(1)$$

$$\nabla p(22) = 4\ \mu(2)\ \nabla\mu(2) + 4\ \Omega(2)\ \nabla\Omega(2) \qquad \text{(B)(A2-68)}$$

$$+ 4\ \sigma_x(2)\ \nabla\sigma_x(2) + 4\ \sigma_y(2)\nabla\sigma_y(2) + 4\ \sigma_z(2)\nabla\sigma_z(2)$$

$$\nabla p(12) = 2\ \mu(1)\ \nabla\mu(2) + 2\ \mu(2)\ \nabla\mu(1)$$

$$+ 2\ \Omega(1)\ \nabla\Omega(2) + 2\ \Omega(2)\ \nabla\Omega(1)$$

$$+ 2\ \sigma_x(1)\ \nabla\sigma_x(2) + 2\ \sigma_y(1)\ \nabla\sigma_y(2) + 2\ \sigma_z(1)\ \nabla\sigma_z(2)$$

$$+ 2\ \sigma_x(2)\ \nabla\sigma_x(1) + 2\ \sigma_y(12)\ \nabla\sigma_y(1) + 2\ \sigma_z(2)\ \nabla\sigma_z(1)$$

(A2-69)

$$\nabla\, \sigma_x(1) = \nabla \left(x_1 * \sum_{k=1}^{4} C_k(P) * A_k(P) \; * e^{-\alpha_k r_1} \right)$$

$$= -\frac{\vec{i}}{2} F_1(P) + x_1 * \frac{\vec{r}_1}{2r_1} \bar{F}_1(P) \qquad \text{(A2-70)}$$

where

$$F_1(P) = \sum_{k=1}^{4} C_k(P) * A_k(P) \; * e^{-\alpha_k r_1} \qquad \text{(A2-71)}$$

$$\bar{F}_1(P) = \sum_{k=1}^{4} C_k(P) * A_k(P) * (-\alpha_k) \; * e^{-\alpha_k r_1} \qquad \text{(A2-72)}$$

$$\nabla\, \sigma_y(1) = \nabla \left(y_1 * \sum_{k=1}^{4} C_k(P) * A_k(P) \; * e^{-\alpha_k r_1} \right)$$

$$= -\frac{\vec{j}}{2} F_1(P) + y_1 * \frac{\vec{r}_1}{2r_1} \bar{F}\,(P) \qquad \text{(A)(A2-73)}$$

$$\nabla\, \sigma_z(1) = \nabla \left(z_1 * \sum_{k=1}^{4} C_k(P) * A_k(P) \; * e^{-\alpha_k r_1} \right)$$

$$= -\frac{\vec{k}}{2} F_1(P) + z_1 * \frac{\vec{r}_1}{2r_1} \bar{F}\,(P) \qquad \text{(B)(A2-73)}$$

$$\nabla\, \sigma_x(2) = \nabla \left(x_2 * \sum_{k=1}^{4} C_k(P) * A_k(P) \; * e^{-\alpha_k r_2} \right)$$

$$= -\frac{\vec{i}}{2} F_2(P) - x_2 * \frac{\vec{r}_2}{2r_2} \bar{F}_2(P) \qquad \text{(A2-74)}$$

where

$$F_2(P) = \sum_{k=1}^{4} C_k(P) * A_k(P) * e^{-\alpha_k r_2} \qquad \text{(A2-75)}$$

$$\bar{F}_2(P) = \sum_{k=1}^{4} C_k(P) * A_k(P) * (-\alpha_k) * e^{-\alpha_k r_2} \qquad \text{(A2-76)}$$

$$\nabla \sigma_y(2) = \nabla \left(y_2 * \sum_{k=1}^{4} C_k(P) * A_k(P) * e^{-\alpha_k r_2} \right)$$

$$= -\frac{\vec{j}}{2} F_2(P) - y_2 * \frac{\vec{r}_2}{2r_2} \bar{F}_2(P) \qquad \text{(A) (A2-77)}$$

$$\nabla \sigma_z(2) = \nabla \left(z_2 * \sum_{k=1}^{4} C_k(P) * A_k(P) * e^{-\alpha_k r_2} \right)$$

$$= -\frac{\vec{k}}{2} F_2(P) - z_2 * \frac{\vec{r}_2}{2r_2} \bar{F}_2(P) \qquad \text{(B) (A2-77)}$$

The second order derivatives for the 2p orbitals of the Ne series are

$$\nabla^2 \sigma_x(1) = \nabla \left(-\frac{\vec{i}}{2} F_1(P) + x_1 * \frac{\vec{r}_1}{2r_1} \bar{F}_1(P) \right)$$

$$= -\frac{x_1}{r_1} \bar{F}_1(P) + -\frac{x_1}{4} \tilde{F}_1(P) \qquad \text{(A2-78)}$$

where

$$\overset{-}{F}_1(P) = \sum_{k=1}^{4} C_k(P) * A_k(P) * (-\alpha_k)^2 * e^{-\alpha_k r_1} \qquad \text{(A2-79)}$$

$$\nabla^2 \sigma_y(1) = \nabla \left(-\frac{\vec{j}}{2} F_1(P) + y_1 * \frac{\vec{r}_1}{2r_1} \bar{F}_1(P) \right)$$

$$= \frac{y_1}{r_1} \bar{F}_1(P) + \frac{y_1}{4} \overset{-}{F}_1(P) \qquad \text{(A)(A2-80)}$$

$$\nabla^2 \sigma_z(1) = \nabla \left(-\frac{\vec{k}}{2} F_1(P) + z_1 * \frac{\vec{r}_1}{2r_1} \bar{F}_1(P) \right)$$

$$= \frac{z_1}{r_1} \bar{F}_1(P) + \frac{z_1}{4} \overset{-}{F}_1(P) \qquad \text{(B)(A2-80)}$$

$$\nabla^2 \sigma_x(2) = - \nabla \left(-\frac{\vec{i}}{2} F_2(P) + x_2 * \frac{\vec{r}_2}{2r_2} \bar{F}_2(P) \right)$$

$$= \frac{x_2}{r_2} \bar{F}_2(P) + \frac{x_2}{4} \overset{-}{F}_2(P) \qquad \text{(A2-81)}$$

where

$$\overset{-}{F}_2(P) = \sum_{k=1}^{4} C_k(P) * A_k(P) * (-\alpha_k)^2 * e^{-\alpha_k r_2} \qquad \text{(A2-82)}$$

$$\nabla^2 \sigma_y(2) = - \nabla \left(-\frac{\vec{j}}{2} F_2(P) + y_2 * \frac{\vec{r}_2}{2r_2} \bar{F}_2(P) \right)$$

$$= \frac{y_2}{r_2} \bar{F}_2(P) + \frac{y_2}{4} \overset{-}{F}_2(P) \qquad \text{(A)(A2-83)}$$

$$\nabla^2\sigma_z(2) = -\nabla\left(-\frac{\vec{k}}{2} F_2(P) + z_2 * \frac{\vec{r}_2^{\,2}}{2r_2} \bar{F}_2(P) \right)$$

$$= -\frac{z_2^2}{r_2} \bar{F}_2(P) + -\frac{z_2^2}{4} \bar{F}_2(P) \qquad \text{(B)(A2-83)}$$

(4). $\nabla^2 P$ (1212) at $r=0$

$r=0$, implies $x=0$, $y=0$ and $z=0$, so it follows that

$$r_1^2 \,\Big|_{r=0} = \left((X+ \frac{x}{2})^2 + (Y+ \frac{y}{2})^2 + (Z+ \frac{z}{2})^2 \right)_{r=0}$$

$$= X^2 + Y^2 + Z^2 = R^2 \qquad \text{(A)(A2-84)}$$

Hence

$$r_1 \,\Big|_{r=0} = R \qquad \text{(B)(A2-84)}$$

$$\vec{r}_1 \,\Big|_{r=0} = \vec{R} \qquad \text{(C)(A2-84)}$$

For similar reasons

$$r_2^2 \,\Big|_{r=0} = \left((X- \frac{x}{2})^2 + (Y- \frac{y}{2})^2 + (Z- \frac{z}{2})^2 \right)_{r=0}$$

$$= X^2 + Y^2 + Z^2 = R^2 \qquad \text{(A)(A2-85)}$$

So

$$r_2 \,\Big|_{r=0} = R \qquad \text{(B)(A2-85)}$$

$$\vec{r}_2 \,\Big|_{r=0} = \vec{R} \qquad \text{(C)(A2-85)}$$

$[\ \nabla^2 P_2(1212)\ ]_{r=0}$ is only the function of R

The above HF orbitals are functions of R only, so the integration over θ and ϕ associated with R can be carried out easily.

$$\Phi(1)\ \Big|_{r=0} = \sum_{i=1}^{4} C_i(1s)*A_i(1s)*e^{-\alpha_i R} = B_R(1s) \qquad \text{(A2-86)}$$

where

$$B\ (1s) = \sum_{i=1}^{4} C_i(1s)*A_i(1s)*e^{-\alpha_i R} \qquad \text{(A2-87)}$$

$$\Phi(2)\ \Big|_{r=0} = \sum_{i=1}^{4} C_i(1s)*A_i(1s)*e^{-\alpha_i R} = B_R(1s) \qquad \text{(A2-88)}$$

$$\Phi(1)\ \Big|_{r=0} = \Phi(2)\ \Big|_{r=0} = B_R(1s) \qquad \text{(A2-89)}$$

The first order derivatives for Φ(1) and Φ(2) at r=0 are

$$\nabla\Phi(1)\ \Big|_{r=0} = \frac{\vec{R}}{2R} \sum_{i=1}^{4} C_i(1s)*A_i(1s)*(-\alpha_i)*e^{-\alpha_i R}$$

$$= \frac{\vec{R}}{2R}\ \bar{B}_R(1s) \qquad \text{(A2-90)}$$

where

$$\bar{B}_R(1s) = \sum_{i=1}^{4} C_i(1s)*A_i(1s)*(-\alpha_i)*e^{-\alpha_i R} \qquad \text{(A2-91)}$$

$$\nabla\Phi(2)\,\Big|_{r=0} = -\frac{\vec{R}}{2R}\sum_{i=1}^{4} C_i(1s)*A_i(1s)*(-\alpha_i)*e^{-\alpha_i R}$$

$$= -\frac{\vec{R}}{2R}\,\bar{B}_R(1s) \qquad \text{(A2-92)}$$

It is clear that

$$\nabla\,\Phi(1)\,\Big|_{r=0} = -\,\nabla\,\Phi(2)\,\Big|_{r=0} = -\frac{\vec{R}}{2R}\,\bar{B}\,(1s) \qquad \text{(A2-93)}$$

A check on the term $\nabla p(12)$:

For He and its isoelectronic series

$$\nabla p(12) = 2\,\Phi(1)\cdot\nabla\Phi(2) + 2\,\Phi(2)\cdot\nabla\Phi(1) \qquad \text{(A2-94)}$$

$$\nabla p(12)\,\Big|_{r=0} = 2\,B_R\overrightarrow{(1s)}\,-\frac{R}{2R}\,\bar{B}_R(1s) + 2\,B_R\overrightarrow{(1s)}\,-\frac{R}{2R}\,\bar{B}_R(1s)$$

$$= 0 \qquad \text{(A2-95)}$$

From

$$\nabla p(21) = \nabla p(12) \qquad \text{(A2-96)}$$

So

$$\nabla p(21)\,\Big|_{r=0} = \nabla p(12)\,\Big|_{r=0} = 0 \qquad \text{(A2-97)}$$

The term $\nabla p(12)\nabla p(21)$ in $\nabla^2 P_2(1212)$ would disappear when $r=0$. And

$$\nabla^2\Phi(1)\ \Big|_{r=0} = -\frac{1}{2R}\ \bar{\bar{B}}_R(1s) + \frac{1}{4}\ \bar{B}_R(1s) \qquad \text{(A2-98)}$$

where

$$\bar{B}_R(1s) = \sum_{i=1}^{4} C_i(1s) * A_i(1s) * (-\alpha_i)^2 \ * e^{-\alpha_i R} \qquad \text{(A2-99)}$$

$$\nabla^2\Phi(2)\ \Big|_{r=0} = -\frac{1}{2R}\ \bar{\bar{B}}_R(1s) + \frac{1}{4}\ \bar{B}_R(1s) \qquad \text{(A2-100)}$$

$$\nabla^2\Phi(1)\ \Big|_{r=0} = \nabla^2\Phi(2)\ \Big|_{r=0} \qquad \text{(A2-101)}$$

In summary

$$\nabla^2 p(12) = \nabla^2 p(21) \qquad \text{(A2-102)}$$

$$\nabla^2 p(11)\ \Big|_{r=0} = \nabla^2 p(22)\ \Big|_{r=0} \qquad \text{(A2-103)}$$

$$\begin{aligned}
\nabla^2 P_2(1212)\ \Big|_{r=0} &= p(11)\cdot\nabla^2 p(22)\Big|_{r=0} + p(22)\cdot\nabla^2 p(11)\Big|_{r=0} \\
&\quad + 2\nabla p(11)\cdot\nabla p(22)\Big|_{r=0} - \nabla p(12)\cdot\nabla p(21)\Big|_{r=0} \\
&\quad - \tfrac{1}{2}\ p(12)\cdot\nabla^2 p(21)\Big|_{r=0} - \tfrac{1}{2}\ p(21)\cdot\nabla^2 p(12)\Big|_{r=0} \\
&= 2\ p(11)\cdot\nabla^2 p(22)\Big|_{r=0} + 2\nabla p(11)\cdot\nabla p(22)\ \Big|_{r=0} \\
&\quad - p(12)\cdot\nabla^2 p(21)\ \Big|_{r=0} \qquad \text{(A2-104)}
\end{aligned}$$

Formulas (A2-102) to (A2-104) also are available for both the Be and the Ne series. For Be and their isoelectronic series the similar forms are

$$\mu(1)\Big|_{r=0}=\sum_{i=1}^{2}C_i(1s)*A_i(1s)\ *e^{-\alpha_i R}+R\ *\sum_{j=3}^{5}C_j(1s)*A_j(1s)\ *e^{-\alpha_j R}$$

(A) (A2-105)

$$\mu(2)\Big|_{r=0}=\sum_{i=1}^{2}C_i(1s)*A_i(1s)\ *e^{-\alpha_i R}+R\ *\sum_{j=3}^{5}C_j(1s)*A_j(1s)\ *e^{-\alpha_j R}$$

(B) (A2-105)

$$\Omega(1)\Big|_{r=0}=\sum_{i=1}^{2}C_i(2s)*A_i(2s)\ *e^{-\alpha_i R}+R\ *\sum_{j=3}^{5}C_j(2s)*A_j(2s)\ *e^{-\alpha_j R}$$

(A) (A2-106)

$$\Omega(2)\Big|_{r=0}=\sum_{i=1}^{2}C_i(2s)*A_i(2s)\ *e^{-\alpha_i R}+R\ *\sum_{j=3}^{5}C_j(2s)*A_j(2s)\ *e^{-\alpha_j R}$$

(B) (A2-106)

It is clear that

$$\mu(1)\ \Big|_{r=0}=\ \mu(2)\ \Big|_{r=0} \qquad \text{(A2-107)}$$

$$\Omega(1)\ \Big|_{r=0}=\ \Omega(2)\ \Big|_{r=0} \qquad \text{(A2-108)}$$

$$\nabla\mu(1)\ \Big|_{r=0}=\ -\frac{\vec{R}}{2R}\ (\ \bar{B}_R(1s)\ +\ D_R(1s)\ +\ R\ *\bar{D}_R(1s)\ )$$

where (A2-109)

$$\bar{B}_R(1s)\ =\sum_{i=1}^{2}C_i(1s)*A_i(1s)*(-\alpha_i)\ \ *e^{-\alpha_i R} \qquad \text{(A2-110)}$$

$$D_R(1s) = \sum_{j=3}^{5} C_j(1s) * A_j(1s) \; * e^{-\alpha_j R} \qquad \text{(A2-111)}$$

$$\bar{D}_R(1s) = \sum_{j=3}^{5} C_j(1s) * A_j(1s) * (-\alpha_j) \; * e^{-\alpha_j R} \qquad \text{(A2-112)}$$

$$\nabla\mu(2) \;\Big|_{r=0} = -\frac{\vec{R}}{2R} \left(\bar{B}_R(1s) + D_R(1s) + R * \bar{D}_R(1s) \right) \qquad \text{(A2-113)}$$

$$\nabla\mu(1) \;\Big|_{r=0} = - \nabla\mu(2) \;\Big|_{r=0} \qquad \text{(A2-114)}$$

$$\nabla\Omega(1) \;\Big|_{r=0} = -\frac{\vec{R}}{2R} \left(\bar{B}_R(2s) + D_R(2s) + R * \bar{D}_R(2s) \right) \qquad \text{(A2-115)}$$

where

$$\bar{B}_R(2s) = \sum_{i=1}^{2} C_i(2s) * A_i(2s) * (-\alpha_i) \; * e^{-\alpha_i R} \qquad \text{(A2-116)}$$

$$D_R(2s) = \sum_{j=3}^{5} C_j(2s) * A_j(2s) \; * e^{-\alpha_j R} \qquad \text{(A2-117)}$$

$$\bar{D}_R(2s) = \sum_{j=3}^{5} C_j(2s) * A_j(2s) * (-\alpha_j) \; * e^{-\alpha_j R} \qquad \text{(A2-118)}$$

$$\nabla\Omega(2) \;\Big|_{r=0} = -\frac{\vec{R}}{2R} \left(\bar{B}_R(2s) + D_R(2s) + R * \bar{D}_R(2s) \right) \qquad \text{(A2-119)}$$

$$\nabla\Omega(1) \;\Big|_{r=0} = - \nabla\Omega(2) \;\Big|_{r=0} \qquad \text{(A2-120)}$$

So we still have

$$\nabla p(21) \;|_{r=0} = \nabla p(12) \;|_{r=0} = 0 \qquad \text{(A2-121)}$$

And for second order derivatives

$$\nabla^2 \mu(1) \;|_{r=0} = \frac{2}{R} \left[\bar{B}_R(1s) + D_R(1s) + R * \bar{D}_R(1s) \right]$$

$$+ \frac{1}{4} \left[\overset{-}{B}_R(1s) + 2\bar{D}_R(1s) + R * \overset{-}{D}_R(1s) \right]$$

(A2-122)

where

$$\overset{-}{B}_R(1s) = \sum_{i=1}^{2} C_i(1s) * A_i(1s) * (-\alpha_i)^2 \; * e^{-\alpha_i R} \qquad \text{(A2-123)}$$

$$\overset{-}{D}_R(1s) = \sum_{j=3}^{5} C_j(1s) * A_j(1s) * (-\alpha_j)^2 \; * e^{-\alpha_j R} \qquad \text{(A2-124)}$$

$$\nabla^2 \mu(2) \;|_{r=0} = \frac{2}{R} \left[\bar{B}_R(1s) + D_R(1s) + R * \bar{D}_R(1s) \right]$$

$$+ \frac{1}{4} \left[\overset{-}{B}_R(1s) + 2\bar{D}_R(1s) + R * \overset{-}{D}_R(1s) \right]$$

(A2-125)

It is clear that

$$\nabla^2 \mu(1) \;|_{r=0} = \nabla^2 \mu(2) \;|_{r=0} \qquad \text{(A2-126)}$$

$$\nabla^2 \Omega(1) \;|_{r=0} = \frac{2}{R} \left[\bar{B}_R(2s) + D_R(2s) + R * \bar{D}_R(2s) \right]$$

$$+ \frac{1}{4} \left[\overset{-}{B}_R(2s) + 2\bar{D}_R(2s) + R * \overset{-}{D}_R(2s) \right]$$

(A2-127)

where

$$\overset{-}{B}_R(2s) = \sum_{i=1}^{2} C_i(2s)*A_i(2s)*(-\alpha_i)^2 \ *e^{-\alpha_i R} \qquad \text{(A2-128)}$$

$$\overset{-}{D}_R(2s) = \sum_{j=3}^{5} C_j(2s)*A_j(2s)*(-\alpha_j)^2 \ *e^{-\alpha_j R} \qquad \text{(A2-129)}$$

$$\nabla^2\Omega(2) \ \Big|_{r=0} = -\frac{2}{R}- \ [\ \bar{B}_R(2s) + D_R(2s) + R \ *\bar{D}_R(2s)]$$

$$+ -\frac{1}{4}- \ [\ \overset{-}{B}_R(2s) + 2\bar{D}_R(2s) + R \ *\overset{-}{D}_R(2s)\ ] \qquad \text{(A2-130)}$$

It is clear that

$$\nabla^2\Omega(1) \ \Big|_{r=0} = \nabla^2\Omega(2) \ \Big|_{r=0} \qquad \text{(A2-131)}$$

All orbitals of the Be series satisfy the equations (A2-102) to (A2-104).

The 1s and 2s orbitals of the Ne isoelectronic series have the same form as the 1s and 2s orbitals of the Be series, only the orbital coefficients are different.

When r=0, the p orbitals of Ne series became

$$\sigma_x(1)\Big|_{r=0} = X \ * \sum_{k=1}^{4} C_k(2P)*A_k(2P) \ *e^{-\alpha_k R} = X*F_R(p) \qquad \text{(A2-132)}$$

where

$$F_R(p) = X \ *\sum_{k=1}^{4} C_k(2P)*A_k(2P) \ *e^{-\alpha_k R} \qquad \text{(A2-133)}$$

$$\sigma_y(1)\Big|_{r=0} = Y*F_R(p) \qquad \text{(A)(A2-134)}$$

$$\sigma_z(1)\big|_{r=0} = Z*F_R(p) \qquad \text{(B) (A2-134)}$$

$$\sigma_x(2)\big|_{r=0} = X * \sum_{k=1}^{4} C_k(2P)*A_k(2P) \; *e^{-\alpha_k R} = X*F_R(p) \qquad \text{(A) (A2-135)}$$

$$\sigma_y(2)\big|_{r=0} = Y*F_R(p) \qquad \text{(B) (A2-135)}$$

$$\sigma_z(2)\big|_{r=0} = Z*F_R(p) \qquad \text{(C) (A2-135)}$$

It is clear that

$$\sigma_x(1)\big|_{r=0} = X*F_R(p) = \sigma_x(2)\big|_{r=0} \qquad \text{(A) (A2-136)}$$

$$\sigma_y(1)\big|_{r=0} = Y*F_R(p) = \sigma_y(2)\big|_{r=0} \qquad \text{(B) (A2-136)}$$

$$\sigma_z(1)\big|_{r=0} = Z*F_R(p) = \sigma_z(2)\big|_{r=0} \qquad \text{(C) (A2-136)}$$

$$\nabla \sigma_x(1)\big|_{r=0} = \frac{\vec{I}}{2} F_R(P) + X * \frac{\vec{R}}{2R} \bar{F}_R(P) \qquad \text{(A2-137)}$$

where

$$\bar{F}_R(P) = \sum_{k=1}^{4} C_k(P)*A_k(P)*(-\alpha_k) \; *e^{-\alpha_k R} \qquad \text{(A2-138)}$$

$$\nabla \sigma_x(2)\big|_{r=0} = \frac{-\vec{I}}{2} F_R(P) - X * \frac{\vec{R}}{2R} \bar{F}_R(P) \qquad \text{(A2-139)}$$

So

$$\nabla \sigma_x(1)\big|_{r=0} = -\frac{\vec{1}}{2} F_R(P) + X * \frac{\vec{R}}{2R} \bar{F}_R(P) = -\nabla \sigma_x(2)\big|_{r=0}$$

(A) (A2-140)

$$\nabla \sigma_y(1)\big|_{r=0} = -\frac{\vec{1}}{2} F_R(P) + Y * \frac{\vec{R}}{2R} \bar{F}_R(P) = -\nabla \sigma_y(2)\big|_{r=0}$$

(B) (A2-140)

$$\nabla \sigma_z(1)\big|_{r=0} = -\frac{\vec{1}}{2} F_R(P) + Y * \frac{\vec{R}}{2R} \bar{F}_R(P) = -\nabla \sigma_z(2)\big|_{r=0}$$

(C) (A2-140)

We still have

$$\nabla p(12)\ \big|_{r=0} = \nabla p(12)\ \big|_{r=0} = 0 \qquad \text{(A2-141)}$$

Also

$$\nabla^2 \sigma_x(1)\big|_{r=0} = -\frac{X}{R} \bar{F}_R(P) + -\frac{1}{4} \bar{F}_R(P) = \nabla^2 \sigma_x(2)\big|_{r=0}$$

(A2-142)

where

$$\bar{F}_R(P) = \sum_{k=1}^{4} C_k(P) * A_k(P) * (-\alpha_k)^2 * e^{-\alpha_k R} \qquad \text{(A2-143)}$$

$$\nabla^2 \sigma_y(1)\big|_{r=0} = -\frac{Y}{R} \bar{F}_R(P) + -\frac{1}{4} \bar{F}_R(P) = \nabla^2 \sigma_y(2)\big|_{r=0}$$

(A) (A2-144)

$$\nabla^2 \sigma_z(1)\big|_{r=0} = -\frac{Z}{R} \bar{F}_R(P) + -\frac{1}{4} \bar{F}_R(P) = \nabla^2 \sigma_z(2)\big|_{r=0}$$

(B) (A2-144)

It is clear that All 2P orbitals satisfy the equations (A2-102) to (A2-104).

APPENDIX (3) KINETIC CORRELATION ENERGY FORMULAS

The general formula shown as (4-16,A-C) in chapter (IV), is

$$Tc = -\frac{1}{2}\int \nabla^2(b(121'2)\cdot P_2(121'2))\Big|_{1'\to 1} d1\ d2 \qquad (A3\text{-}1)$$

$$Tc(1) = -\frac{1}{2}\int b(121'2)\cdot \nabla^2 P_2(121'2)\Big|_{1'\to 1} d1\ d2 \qquad (A)(A3\text{-}2)$$

$$Tc(2) = -\int \nabla b(121'2)\cdot \nabla_2 P\ (121'2)\Big|_{1'\to 1} d1\ d2 \qquad (B)(A3\text{-}2)$$

$$Tc(3) = -\frac{1}{2}\int P_2(121'2)\cdot \nabla^2 b(121'2)\Big|_{1'\to 1} d1\ d2 \qquad (C)(A3\text{-}2)$$

$$Tc = Tc(1) + Tc(2) + Tc(3) \qquad (A3\text{-}3)$$

(1) Basic variables

It is convenient for the calculation of Tc(1) to put the system into the coordinates (2); and for the calculation of Tc(2) and Tc(3) to put the system into the coordinates (1) in Appendix (1). The 6 dimensional integration for two bodies may be simplified to 3 dimensional numerical integration and the formula (A3-2) becomes

$$Tc(1) = -\frac{1}{2}\, 8\pi^2 \int_{-1}^{1}\int_{0}^{\infty}\int_{0}^{\infty} b(121'2)\cdot \nabla^2 P_2(121'2)\Big|_{1'\to 1} dr_1 dr_2 d\cos\theta' \qquad (A)(A3\text{-}4)$$

$$Tc(2) = - 8\pi^2 \int_{-1}^{1}\int_{0}^{\infty}\int_{0}^{\infty} \nabla b(121'2)\cdot\nabla P_2(121'2)\Big|_{1'\rightarrow 1} dR\ dr\ d\cos\theta \qquad (B)(A3\text{-}4)$$

$$Tc(3) = - \tfrac{1}{2}\, 8\pi^2 \int_{-1}^{1}\int_{0}^{\infty}\int_{0}^{\infty} P_2(121'2)\cdot\nabla^2 b(121'2)\Big|_{1'\rightarrow 1} dR\ dr\ d\cos\theta \qquad (C)(A3\text{-}4)$$

The details of the transformation are in Appendix (1). The selection of the coordinates (1) or (2) is based on the fact that more variables in the denominator may be canceled in the coordinates chosen before the numerical integration, so that the integration of the formula (A3-4) can be completed more easyly with our 3D Simpson numerical integration program.

Some of the basic variables are

$$\nabla = \vec{i}\,\frac{\partial}{\partial x_1} + \vec{j}\,\frac{\partial}{\partial y_1} + \vec{k}\,\frac{\partial}{\partial z_1} \qquad (A)(A3\text{-}5)$$

$$\nabla^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \qquad (B)(A3\text{-}5)$$

$$\vec{r}_1 = \vec{i}x_1 + \vec{j}y_1 + \vec{k}z_1 \qquad (A)(A3\text{-}6)$$

$$\vec{R} = \tfrac{1}{2}\,(\vec{r}_1 + \vec{r}_2) \qquad (B)(A3\text{-}6)$$

$$\vec{r} = \vec{r}_1 - \vec{r}_2 \qquad \text{(C) (A3-6)}$$

(2) Derivatives of the for basic variables

$$\nabla r_1 = \nabla [x_1^2 + y_1^2 + z_1^2]^{\frac{1}{2}} = [\vec{i}x_1 + \vec{j}y_1 + \vec{k}z_1] \cdot [x_1^2 + y_1^2 + z_1^2]^{-\frac{1}{2}}$$

$$= \frac{\vec{r}_1}{r_1} \qquad \text{(A) (A3-7)}$$

$$\nabla R = \nabla \left(\tfrac{1}{2} [(x_1+x_2)^2 + (y_1+y_2)^2 + (z_1+z_2)^2] \right)^{\frac{1}{2}}$$

$$= \frac{1}{2} \frac{2[\vec{i}(x_1+x_2) + \vec{j}(y_1+y_2) + \vec{k}(z_1+z_2)]}{2[(x_1+x_2)^2 + (y_1+y_2)^2 + (z_1+z_2)^2]^{\frac{1}{2}}}$$

$$= \frac{\vec{R}}{2R} \qquad \text{(B) (A3-7)}$$

$$\nabla r = \nabla [(x_1-x_2)^2 + (y_1-y_2)^2 + (z_1-z_2)^2]^{\frac{1}{2}}$$

$$= \frac{\vec{i}(x_1-x_2) + \vec{j}(y_1-y_2) + \vec{k}(z_1-z_2)}{[(x_1-x_2)^2 + (y_1-y_2)^2 + (z_1-z_2)^2]^{\frac{1}{2}}}$$

$$= \frac{\vec{r}}{r} \qquad \text{(C) (A3-7)}$$

$$\nabla \vec{r}_1 = \nabla [\vec{i}x_1 + \vec{j}y_1 + \vec{k}z_1] = 3 \qquad \text{(A) (A3-8)}$$

$$\nabla \vec{R} = \nabla \tfrac{1}{2} [\vec{i}(x_1+x_2) + \vec{j}(y_1+y_2) + \vec{k}(z_1+z_2)]$$

$$= \frac{3}{2} \tag*{(B)(A3-8)}$$

$$\nabla \vec{r} = \nabla [\vec{i}(x_1-x_2) + \vec{j}(y_1-y_2) + \vec{k}(z_1-z_2)]$$

$$= 3 \tag*{(C)(A3-8)}$$

$$\vec{R}\cdot\vec{r} = Rr\cdot\cos\theta \tag*{(A)(A3-9)}$$

$$\vec{r}_1\cdot\vec{r}_2 = r_1 r_2 \cos\theta' \tag*{(B)(A3-9)}$$

$$\vec{R}\cdot\vec{r}_1 = \vec{R}\cdot(\vec{R} + \frac{\vec{r}}{2}) = R^2 + \tfrac{1}{2} Rr\cdot\cos\theta \tag*{(A)(A3-10)}$$

$$\vec{R}\cdot\vec{r}_1 = \tfrac{1}{2}(\vec{r}_1 + \vec{r}_2)\cdot\vec{r}_1 = \tfrac{1}{2} (r_1^2 + r_1 r_2 \cos\theta') \tag*{(B)(A3-10)}$$

$$\vec{r}\cdot\vec{r}_1 = \vec{r}\cdot(\vec{R} + \frac{\vec{r}}{2}) = Rr\cdot\cos\theta + \tfrac{1}{2} r^2 \tag*{(A)(A3-11)}$$

$$\vec{r}\cdot\vec{r}_1 = (\vec{r}_1 - \vec{r}_2)\cdot\vec{r}_1 = r_1^2 - r_1 r_2 \cos\theta' \tag*{(B)(A3-11)}$$

For convenience put

$$V_R = \frac{\vec{r}_1}{r_1} \cdot \frac{\vec{R}}{R} = \frac{1}{r_1} (R + \tfrac{1}{2} r\cdot\cos\theta) \tag*{(A)(A3-12)}$$

$$V_R = \frac{\vec{r}_1}{r_1} \cdot \frac{\vec{R}}{R} = \frac{1}{2R}\,(r_1 + r_2\cos\theta') \qquad \text{(B)(A3-12)}$$

$$V_r = \frac{\vec{r}_1}{r_1} \cdot \frac{\vec{r}}{r} = \frac{1}{r_1}\,(R\cdot\cos\theta + \tfrac{1}{2}\,r) \qquad \text{(A)(A3-13)}$$

$$V_r = \frac{\vec{r}_1}{r_1} \cdot \frac{\vec{r}}{r} = \frac{1}{r}\,(r_1 - r_2\cos\theta') \qquad \text{(B)(A3-13)}$$

$$\nabla^2 r_1 = \nabla\,\frac{\vec{r}_1}{r_1} = \frac{1}{r_1}\,\nabla\,\vec{r}_1 + \vec{r}_1\nabla\,\frac{1}{r_1} = \frac{3}{r_1} - \frac{\vec{r}_1}{r_1^2}\cdot\frac{\vec{r}_1}{r_1}$$

$$= \frac{2}{r_1} \qquad \text{(A)(A3-14)}$$

$$\nabla^2 R = \nabla\,\frac{\vec{R}}{2R} = \frac{1}{2R}\,\nabla\,\vec{R} + \vec{R}\,\nabla\,\frac{1}{2R} = \frac{3}{4R} - \frac{\vec{R}}{2R^2}\,\frac{\vec{R}}{2R}$$

$$= \frac{1}{2R} \qquad \text{(B)(A3-14)}$$

$$\nabla^2 r = \nabla\,\frac{\vec{r}}{r} = \frac{1}{r}\,\nabla\,\vec{r} + \vec{r}\,\nabla\,\frac{1}{r} = \frac{3}{r} - \frac{\vec{r}}{r^2}\,\frac{\vec{r}}{r}$$

$$= \frac{2}{r} \qquad \text{(C)(A3-14)}$$

(2) Derivatives of basis functions of the He atom and its isoelectronic series

$$\Phi(1) = \sum_{i=1}^{4} C_i A_i e^{-\alpha_i r_1} \qquad \text{(A)(A3-15)}$$

$$\nabla \Phi(1) = \nabla \left(\sum_{i=1}^{4} C_i A_i e^{-\alpha_i r_1} \right)$$

$$= \frac{\vec{r}_1}{r_1} \sum_{i=1}^{4} C_i A_i (-\alpha_i) e^{-\alpha_i r_1} \qquad \text{(B)(A3-15)}$$

$$\nabla^2 \Phi(1) = \nabla \left(\frac{\vec{r}_1}{r_1} \sum_{i=1}^{4} C_i A_i (-\alpha_i) e^{-\alpha_i r_1} \right) \qquad \text{(C)(A3-15)}$$

$$= \frac{\vec{r}_1}{r_1} \nabla \left(\sum_{i=1}^{4} C_i A_i (-\alpha_i) e^{-\alpha_i r_1} \right) + \left(\sum_{i=1}^{4} C_i A_i (-\alpha_i) e^{-\alpha_i r_1} \right) \nabla \frac{\vec{r}}{r_1}$$

$$= \left(\sum_{i=1}^{4} C_i A_i (-\alpha_i)^2 \, e^{-\alpha_i r_1} \right) + \frac{2}{r_1} \left(\sum_{i=1}^{4} C_i A_i (-\alpha_i) e^{-\alpha_i r_1} \right)$$

For convenience, put

$$B(1) = \sum_{i=1}^{4} C_i A_i e^{-\alpha_i r_1} \qquad \text{(A)(A3-16)}$$

$$\bar{B}(1) = \sum_{i=1}^{4} C_i A_i (-\alpha_i) \, e^{-\alpha_i r_1} \qquad \text{(B)(A3-16)}$$

$$\overset{-}{B}(1) = \sum_{i=1}^{4} C_i A_i (-\alpha_i)^2 e^{-\alpha_i r_1} \qquad \text{(C)(A3-16)}$$

$$\nabla \Phi(1) = \frac{\vec{r}_1}{r_1} \bar{B}(1) \qquad \text{(A)(A3-17)}$$

$$\nabla^2\Phi(1) = \bar{B}(1) + \frac{2}{r_1}\bar{\bar{B}}(1) \qquad \text{(B) (A3-17)}$$

$$\Phi(R) = \sum_{i=1}^{4} C_i A_i e^{-\alpha_i R} \qquad \text{(A) (A3-18)}$$

$$\nabla\Phi(R) = \nabla\left(\sum_{i=1}^{4} C_i A_i e^{-\alpha_i R}\right)$$

$$= \frac{\vec{R}}{2R}\sum_{i=1}^{4} C_i A_i (-\alpha_i) e^{-\alpha_i R} \qquad \text{(B) (A3-18)}$$

$$\nabla^2\Phi(R) = \nabla\left(\frac{\vec{R}}{2R}\sum_{i=1}^{4} C_i A_i (-\alpha_i) e^{-\alpha_i R}\right) \qquad \text{(C) (A3-18)}$$

$$= \frac{\vec{R}}{2R}\nabla\left(\sum_{i=1}^{4} C_i A_i (-\alpha_i) e^{-\alpha_i R}\right) + \left(\sum_{i=1}^{4} C_i A_i (-\alpha_i) e^{-\alpha_i R}\right)\nabla\frac{\vec{R}}{2R}$$

$$= \frac{1}{4}\left(\sum_{i=1}^{4} C_i A_i (-\alpha_i)^2 e^{-\alpha_i R}\right) + \frac{1}{2R}\left(\sum_{i=1} C_i A_i (-\alpha_i) e^{-\alpha_i R}\right)$$

For convenience, put

$$B(R) = \sum_{i=1}^{4} C_i A_i e^{-\alpha_i R} \qquad \text{(A) (A3-19)}$$

$$\bar{\bar{B}}(R) = \sum_{i=1}^{4} C_i A_i (-\alpha_i)\, e^{-\alpha_i R} \qquad \text{(B) (A3-19)}$$

$$\bar{B}(R) = \sum_{i=1}^{4} C_i A_i (-\alpha_i)^2 e^{-\alpha_i R} \qquad \text{(C) (A3-19)}$$

$$\nabla\Phi(R) = \frac{\vec{R}}{2R}\bar{\bar{B}}(R) \qquad \text{(A) (A3-20)}$$

$$\nabla^2\Phi(R) = \frac{1}{4}\,\tilde{B}(R) + \frac{1}{2R}\,\bar{B}(R) \qquad \text{(B) (A3-20)}$$

$$p(R) = 2\Phi(R)\Phi(R) \qquad \text{(A) (A3-21)}$$

$$\nabla p(R) = \nabla(2\Phi(R)\Phi(R)) = 4\Phi(R)\nabla\Phi(R)$$

$$= 2\Phi(R)\bar{B}(R)\,\frac{\vec{R}}{R}$$

$$= \bar{p}(R)\,\frac{\vec{R}}{R} \qquad \text{(B) (A3-21)}$$

where

$$\bar{p}(R) = 2\Phi(R)\bar{B}(R) \qquad \text{(A3-22)}$$

$$\nabla^2 p(R) = \nabla\,(4\Phi(R)\nabla\Phi(R)) = 4\Phi(R)\nabla^2\Phi(R) + 4[\nabla\Phi(R)]^2$$

$$= \Phi(R)\,[\tilde{B}(R) + \frac{2}{R}\,\bar{B}(R)] + [\bar{B}(R)]^2 \qquad \text{(A) (A3-23)}$$

put

$$\tilde{p}(R) = \nabla^2 p(R) \qquad \text{(B) (A3-23)}$$

$$\nabla p(R)^{1/3} = \frac{1}{3}\,p(R)^{-2/3}\nabla p(R) = \frac{p(R)^{1/3}}{3p(R)}\,\nabla p(R)$$

$$= \frac{\vec{R}}{R}\,\frac{2\Phi(R)\bar{B}(R)}{3p(R)}\,p(R)^{1/3}$$

$$= \frac{\vec{R}}{R}\,p'(R)\cdot p(R)^{1/3} \qquad \text{(A3-25)}$$

where

$$p'(R) = \frac{2\Phi(R)\bar{B}(R)}{3p(R)} \qquad \text{(A) (A3-26)}$$

$$\nabla\ p'(R) = \nabla\left(\frac{2\Phi(R)\bar{B}(R)}{3p(R)}\right)$$

$$= \frac{2\bar{B}(R)}{3p(R)}\ \nabla\Phi(R) + \frac{2\Phi(R)}{3p(R)}\ \nabla\bar{B}(R) + \frac{2\Phi(R)\bar{B}(R)}{3}\ \nabla\ \frac{1}{p(R)}$$

$$= \frac{\vec{R}}{R}\ \left\{\ \frac{[\bar{B}(R)]^2}{3p(R)} + \frac{\Phi(R)\bar{B}(R)}{3p(R)} + \frac{-2[\bar{B}(R)]^2}{3p(R)}\ \right\}$$

$$= \frac{\vec{R}}{R}\ \frac{1}{3p(R)}\ \left\{\ \Phi(R)\bar{B}(R)-[\bar{B}(R)]^2\ \right\}$$

$$= \frac{\vec{R}}{R}\ p''(R) \qquad \text{(B) (A3-26)}$$

where

$$p''(R) = \frac{1}{3p(R)}\ \left\{\ \Phi(R)\bar{B}(R)-[\bar{B}(RR)]^2\ \right\} \qquad \text{(A3-27)}$$

$$\beta = q\ p(R)^{1/3} \qquad \text{(A) (A3-28)}$$

$$\nabla\beta = q\ \nabla p(R)^{1/3} = q\cdot p(R)^{1/3}p'(R)\ \frac{\vec{R}}{R}$$

$$= \frac{\vec{R}}{R}\ \beta p'(R) \qquad \text{(B) (A3-28)}$$

$$[\nabla\beta]^2 = \beta^2\,[p'(R)]^2 \qquad \text{(C) (A3-28)}$$

$$\nabla^2 \beta = \nabla\left\{ \frac{\vec{R}}{R} \beta p'(R) \right\} \qquad \text{(D)(A3-28)}$$

$$= \frac{\vec{R}}{R} p'(R) \nabla\beta + \frac{\vec{R}}{R} \beta \nabla p'(R) + \beta p'(R) \nabla \frac{\vec{R}}{R}$$

$$= \beta [p'(R)]^2 + \beta p''(R) + \beta p'(R) \frac{1}{R}$$

$$= \beta \left\{ p''(R) + [p'(R)]^2 + p'(R) \frac{1}{R} \right\}$$

(3) Derivatives of various functional and density functions

$$p(11') = 2\Phi(1)\Phi(1') \qquad \text{(A)(A3-29)}$$

$$p(12) = 2\Phi(1)\Phi(2) \qquad \text{(B)(A3-29)}$$

$$P_2(121'2) = p(11')p(22) - \tfrac{1}{2}\, p(12)p(21')$$

$$= 2\Phi(1)\Phi(1') \cdot p(22) - \tfrac{1}{2} \cdot 2\Phi(1)\Phi(2) \cdot p(21')$$

$$= \{2\Phi(1') \cdot p(22) - \Phi(2) \cdot p(21')\} \cdot \Phi(1) \qquad \text{(A)(A3-30)}$$

$$\nabla P_2(121'2) = \{2\Phi(1') \cdot p(22) - \Phi(2) \cdot p(21')\}\ \nabla\Phi(1)$$

$$= \frac{\vec{r}_1}{r_1} \bar{B}(1)\ \{2\Phi(1') \cdot p(22) - \Phi(2) \cdot p(21')\} \qquad \text{(B)(A3-30)}$$

$$\nabla^2 P_2(121'2) = \{2\Phi(1') \cdot p(22) - \Phi(2) \cdot p(21')\}\ \nabla^2\Phi(1)$$

$$= \{2\Phi(1') \cdot p(22) - \Phi(2) \cdot p(21')\}\ \nabla\left[\frac{\vec{r}_1}{r_1} \bar{B}(1)\right]$$

$$= \left[\bar{B}(1) + \frac{2}{r_1} \bar{B}(1)\right] \{2\Phi(1') \cdot p(22) - \Phi(2) \cdot p(21')\} \qquad \text{(C)(A3-30)}$$

$$\phi(12) = [1-\epsilon(R)(1+ \frac{r}{2})]\cdot e^{-\beta^2 r^2} \tag*{(A) (A3-31)}$$

$$\nabla\phi(12) = \nabla \{[1-\epsilon(R)(1+ \frac{r}{2})]e^{-\beta^2 r^2}\}$$

$$= [1-\epsilon(R)(1+ \frac{r}{2})]\nabla e^{-\beta^2 r^2} - e^{-\beta^2 r^2}\nabla[\epsilon(R)(1+ \frac{r}{2})] \tag*{(B) (A3-31)}$$

$$\nabla^2\phi(12) = [1-\epsilon(R)(1 + \frac{r}{2})]\ \nabla^2 e^{-\beta^2 r^2}$$

$$+ 2\nabla[1-\epsilon(R)(1+ \frac{r}{2})]\cdot\nabla e^{-\beta^2 r^2} + e^{-\beta^2 r^2}\ \nabla^2[1-\epsilon(R)(1 + \frac{r}{2})] \tag*{(C) (A3-31)}$$

$$\nabla\ [\beta^2 r^2] = 2\beta r[r\nabla\beta + \beta\nabla r]$$

$$= 2\beta^2 r\ [rp'(R)\ \frac{\vec{R}}{R} + \frac{\vec{r}}{r}] \tag*{(A3-32)}$$

$$\nabla\ e^{-\beta^2 r^2} = e^{-\beta^2 r^2}\nabla[-\beta^2 r^2] = -2\beta r\cdot e^{-\beta^2 r^2}[r\nabla\beta + \beta\nabla r]$$

$$= -2\beta r\cdot e^{-\beta^2 r^2}[r\beta p'(R)\ \frac{\vec{R}}{R} + \beta\ \frac{\vec{r}}{r}\ ] \tag*{(A3-33)}$$

Put

$$L = (\nabla[-\beta^2 r^2])^2 \tag*{(A) (A3-34)}$$

$$(\nabla[-\beta^2 r^2])^2 = (2\beta^2 r[rp'(R)\ \frac{\vec{R}}{R} + \frac{\vec{r}}{r}])^2$$

$$= 4\beta^4 r^2([rp'(R)]^2 + 2rp'(R)\cdot\cos\theta + 1) \tag*{(B) (A3-34)}$$

Put

$$M = \nabla^2[\beta^2 r^2] \qquad \text{(A)(A3-35)}$$

$$\nabla^2[\beta^2 r^2] = r^2\nabla^2\beta^2 + 2\nabla\beta^2\nabla r^2 + \beta^2\nabla^2 r^2$$

$$= 2r^2(\beta\nabla^2\beta + [\nabla\beta]^2) + 8\beta r\nabla\beta\nabla r + 2\beta^2(r\nabla^2 r + [\nabla r]^2)$$

$$= 2\beta^2 r^2 \left(p''(R) + [p'(R)]^2 + \frac{1}{R} p'(R) \right)$$

$$+ 2\beta^2 r^2 [p'(R)]^2 + 8\beta^2 r\cdot p'(R)\cdot\cos\theta + 6\beta^2$$

$$= 2\beta^2 r^2 \left(p''(R) + 2[p'(R)]^2 + \frac{1}{R} p'(R) \right)$$

$$+ 8\beta^2 r\cdot p'(R)\cdot\cos\theta + 6\beta^2 \qquad \text{(B)(A3-35)}$$

$$\nabla^2 e^{-\beta^2 r^2} = \nabla\left(e^{-\beta^2 r^2}\nabla[-\beta^2 r^2] \right)$$

$$= e^{-\beta^2 r^2}\nabla^2[-\beta^2 r^2] + \nabla[-\beta^2 r^2]\cdot\nabla e^{-\beta^2 r^2}$$

$$= -M\cdot e^{-\beta^2 r^2} + (\nabla[-\beta^2 r^2])^2\cdot e^{-\beta^2 r^2}$$

$$= [L-M]\cdot e^{-\beta^2 r^2} \qquad \text{(A3-36)}$$

$$[1-\epsilon(R)(1+\frac{r}{2})]\cdot\nabla^2 e^{-\beta^2 r^2}$$

$$= [1-\epsilon(R)(1+\frac{r}{2})]\cdot[L-M]\cdot e^{-\beta^2 r^2} \qquad \text{(A3-37)}$$

$$\epsilon(R) = \frac{u\cdot\sqrt{\pi}\beta}{t+\sqrt{\pi}\beta} \qquad \text{(A)(A3-38)}$$

$$\nabla \epsilon(R) = \nabla \frac{u \cdot \sqrt{\pi\beta}}{t + \sqrt{\pi\beta}} = u \frac{(t+\sqrt{\pi\beta})\nabla[\sqrt{\pi\beta}] - \sqrt{\pi\beta}\nabla(t+\sqrt{\pi\beta})}{(t+\sqrt{\pi\beta})^2}$$

$$= u \frac{t\nabla[\sqrt{\pi\beta}]}{(t+\sqrt{\pi\beta})^2} = u \frac{t\sqrt{\pi\beta}p'(R)}{(t+\sqrt{\pi\beta})^2} \frac{\vec{R}}{R}$$

$$= \frac{\vec{R}}{R} \frac{ut\sqrt{\pi\beta}}{(t+\sqrt{\pi\beta})^2} p'(R) \qquad \text{(B)(A3-38)}$$

Put

$$W = \nabla^2 \epsilon(R) \qquad \text{(A)(A3-39)}$$

$$\nabla^2 \epsilon(R) = \nabla^2\left(\frac{u\sqrt{\pi\beta}}{(t+\sqrt{\pi\beta})^2} \right) = \nabla \left(\frac{ut\nabla[\sqrt{\pi\beta}]}{(t+\sqrt{\pi\beta})^2} \right)$$

$$= \frac{(t+\sqrt{\pi\beta})^2 ut\nabla^2[\sqrt{\pi\beta}] - ut\nabla[\sqrt{\pi\beta}]\nabla(t+\sqrt{\pi\beta})^2}{(t+\sqrt{\pi\beta})^4}$$

$$= ut \frac{(t+\sqrt{\pi\beta})\nabla^2[\sqrt{\pi\beta}] - 2(\nabla\sqrt{\pi\beta})^2}{(t+\sqrt{\pi\beta})^3}$$

$$= ut \frac{(t+\sqrt{\pi\beta})\sqrt{\pi\beta}\ \{p''(R)+[p'(R)]^2+p'(R)\frac{1}{R}\} - 2\pi\beta^2[p'(R)]^2}{(t+\sqrt{\pi\beta})^3}$$

(B)(A3-39)

$$\nabla [1-\epsilon(R)(1+\frac{r}{2})] = -\nabla[\epsilon(R)(1+\frac{r}{2})] \qquad \text{(A)(A3-40)}$$

$$= -(1+\frac{r}{2})\ \nabla\epsilon(R) - \epsilon(R)\ \nabla(1+\frac{r}{2})$$

$$= -(1+\frac{r}{2})\ \frac{\vec{R}}{R}\ \frac{ut\sqrt{\pi\beta}}{(t+\sqrt{\pi\beta})^2} p'(R) - \tfrac{1}{2}\epsilon(R)\ \frac{\vec{r}}{r}$$

$$\nabla^2[1-\epsilon(R)(1+\frac{r}{2})] \qquad \text{(B) (A3-40)}$$

$$= -(1+\frac{r}{2})\,\nabla^2\epsilon(R) - 2\nabla\epsilon(R)\nabla(1+\frac{r}{2}) - \epsilon(R)\,\nabla^2(1+\frac{r}{2})$$

$$= -(1+\frac{r}{2})\cdot W - 2\,\frac{\vec{R}}{R}\,\frac{ut\sqrt{\pi}\beta}{(t+\sqrt{\pi}\beta)^2}\,p'(R)\cdot\frac{\vec{r}}{2r} - \frac{1}{r}\,\epsilon(R)$$

$$= -(1+\frac{r}{2})\cdot W - \frac{ut\sqrt{\pi}\beta}{(t+\sqrt{\pi}\beta)^2}\,p'(R)\cdot\cos\theta - \frac{1}{r}\,\epsilon(R)$$

$$e^{-\beta^2 r^2}\,\nabla^2[1-\epsilon(R)(1+\frac{r}{2})] \qquad \text{(A3-41)}$$

$$= -\,e^{-\beta^2 r^2}\{\ (1+\frac{r}{2})\cdot W + \tfrac{1}{2}\,\frac{ut\sqrt{\pi}\beta}{(t+\sqrt{\pi}\beta)^2}\,p'(R)\cdot\cos\theta + \epsilon(R)\ \}$$

$$2\nabla[1-\epsilon(R)(1+\frac{r}{2})]\cdot\nabla e^{-\beta^2 r^2} \qquad \text{(A3-42)}$$

$$= 2\ \{\ -\ (1+\frac{r}{2})\ \frac{\vec{R}}{R}\ \frac{ut\sqrt{\pi}\beta}{(t+\sqrt{\pi}\beta)^2}\ p'(R) - \tfrac{1}{2}\epsilon(R)\ \frac{\vec{r}}{r}\ \}$$

$$\cdot\ \{\ -2\beta r\cdot e^{-\beta^2 r^2}[r\beta p'(R)\ \frac{\vec{R}}{R} + \beta\ \frac{\vec{r}}{r}\ ]\ \}$$

$$= 4\beta r e^{-\beta^2 r^2}\{\beta r\cdot[p'(R)]^2\,(1+\frac{r}{2})\ \frac{ut\sqrt{\pi}\beta}{(t+\sqrt{\pi}\beta)^2} + \tfrac{1}{2}\beta\epsilon(R)$$

$$+\ \tfrac{1}{2}\ \beta r\cdot p'(R)\cdot\epsilon(R)\cdot\cos\theta$$

$$+\ \beta\cdot p'(R)\cdot(1+\frac{r}{2})\ \frac{ut\sqrt{\pi}\beta}{(t+\sqrt{\pi}\beta)^2}\ \cos\theta\ \}$$

(4). Summary

$$\nabla^2\{\ b(121'2)\cdot P_2(121'2)\ \} \tag{A3-43}$$

$$= b(121'2)\ \nabla^2 P_2(121'2) + P_2(121'2)\ \nabla^2 b(121'2)$$

$$+ 2\ \nabla b(121'2)\ \nabla P_2(121'2)$$

$$b(121'2) = \phi(12)\phi(1'2) - \phi(12) - \phi(1'2)$$

$$P_2(121'2) = p(11')p(22) - \tfrac{1}{2}\ p(12)p(21')$$

$$= \Phi(1)\{\ 2\Phi(1')p(22) - \Phi(2)p(21')\ \}$$

$$b(121'2)\ \nabla^2 P_2(121'2) \tag{A3-44}$$

$$= b(121'2)\cdot\{2\Phi(1')p(22) - \Phi(2)p(21')\}\ \nabla^2\Phi(1)$$

$$= b(121'2)\cdot[\bar{\dot{B}}(1) + \frac{2}{r}\ \bar{B}(1)]\ \{2\Phi(1')p(22) - \Phi(2)p(21')\}$$

$$P_2(121'2)\cdot\nabla^2 b(121'2) = P_2(121'2)\cdot\{\ \phi(1'2) -1\ \}\ \nabla^2\phi(12) \tag{A3-45}$$

$$\nabla^2\phi(12) = [1-\epsilon(R)(1 + \frac{r}{2})]\ \nabla^2 e^{-\beta^2 r^2} \tag{A3-46}$$

$$+ 2\nabla[1-\epsilon(R)(1+ \frac{r}{2})]\cdot\nabla e^{-\beta^2 r^2} + e^{-\beta^2 r^2}\ \nabla^2[1-\epsilon(R)(1 + \frac{r}{2})]$$

$$= [1- \epsilon(R)(1+ \frac{r}{2})]\cdot[L-M]\cdot e^{-\beta^2 r^2}$$

$$+ 4\beta r e^{-\beta^2 r^2}\{\beta r\cdot[p'(R)]^2(1+ \frac{r}{2}) \frac{ut\sqrt{\pi\beta}}{(t+\sqrt{\pi\beta})^2} + \tfrac{1}{2}\beta\epsilon(R)$$

$$+ \tfrac{1}{2}\beta r\cdot p'(R)\cdot\epsilon(R)\cdot\cos\theta + \beta\cdot p'(R)\cdot(1+ \frac{r}{2}) \frac{ut\sqrt{\pi\beta}}{(t+\sqrt{\pi\beta})}\cos\theta \}$$

$$- e^{-\beta^2 r^2}\{ (1+ \frac{r}{2})\cdot W + \frac{ut\sqrt{\pi\beta}}{(t+\sqrt{\pi\beta})^2} p'(R)\cdot\cos\theta + \frac{1}{r}\epsilon(R) \}$$

$$2 \nabla b(121'2) \nabla P_2(121'2) \qquad \text{(A3-47)}$$

$$= 2 \{\phi(1'2) -1\}\nabla\phi(12)\cdot\{2\Phi(1')p(22) - \Phi(2)p(21')\}\nabla\Phi(1)$$

$$= 2 \{\phi(1'2) -1\}\cdot\{2\Phi(1')p(22)-\Phi(2)p(21')\}\cdot\nabla\phi(12)\cdot\nabla\Phi(1)$$

$$\nabla \phi(12)\cdot\nabla\Phi(1) \qquad \text{(A3-48)}$$

$$= [1-\epsilon(R)(1+ \frac{r}{2})]\nabla e^{-\beta^2 r^2} - e^{-\beta^2 r^2}\nabla[\epsilon(R)(1+ \frac{r}{2})] \nabla\Phi(1)$$

$$= \{ -2\beta r\cdot e^{-\beta^2 r^2}[r\beta p'(R) \frac{\vec{R}}{R} + \beta \frac{\vec{r}}{r}]\cdot[1-\epsilon(R)(1+ \frac{r}{2})]$$

$$- e^{-\beta^2 r^2}[(1+ \frac{r}{2}) \frac{\vec{R}}{R} \frac{ut\sqrt{\pi\beta}}{(t+\sqrt{\pi\beta})^2} p'(R) + \tfrac{1}{2}\epsilon(R) \frac{\vec{r}}{r}]\} \frac{\vec{r}_1}{r_1}B(1)$$

$$= - e^{-\beta^2 r^2}\cdot\bar{B}(1) \{ 2\beta^2 r[rp'(R)\cdot V_R + V_r]\cdot[1-\epsilon(R)(1+ \frac{r}{2})]$$

$$+ [(1+ \frac{r}{2}) \frac{ut\sqrt{\pi\beta}}{(t+\sqrt{\pi\beta})^2} p'(R)\cdot V_R + \tfrac{1}{2}\epsilon(R)\cdot V_r]\}$$

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