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by

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Abstract

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First- and second order density matrices approximately N-representable by a correlated determinant wavefunction, whose reference state is a single determinant delivering the exact density, are derived. This density-matrix formalism is applied to the calculation of the correlation energy via a formula which includes both a kinetic energy contribution and a potential energy contribution. The single determinant of x-ray orbitals for the beryllium atom is used in a test calculation that yields 65 per cent of the correlation energy in a simple zeroth-order approximation. Extension of the calculations using a Hartree-Fock reference stateis carried out for helium and beryllium atoms and for series of ions isoelectronic with them. For beryllium, the accuracy of the Hartree-Fock reference state results is comparable to the x-ray orbitals reference state case. The results for the series of ions are of poorer accuracy as the nuclear charge charge increases. Also, the empirical formula of Colle and Salvetti for the calculation of the correlation energy is appliedto the series of ions isoelectronic with helium and

beryllium. The accuracy of the results decreases with the increasing of the nuclear charge in both series.

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CHAPTER 1 INTRODUCTION

The single crystal coherent x-ray diffraction experiment gives an image of the electron density of crystalline solids. The Hohenberg and Kohn (HK) theorem(1) states that the many-particle ground state is a unique functional of the electronic density or, in other words, that the electron density contains all the information necessary to evaluate every electronic property of the system. Based on these two fundamental facts, a method to extract quantum mechanically valid density matrices from crystallographic data has been developed.(2-9) Properties calculated with a single determinant of x-ray orbitals for some test systems are remarkably good.(10-13)

In this thesis we derive density matrices N-representable by a correlated-determinant wavefunction whose reference state is the x-ray orbitals single determinant, and we use this density-matrix formalism for the calculation of the correlation energy.

A review of the quantum model of coherent x-ray diffraction and a summarized account of the correlation problem will introduce some of the ideas that are relevant in our approach to the correlation energy.

When a beam of x-rays shines on a crystal, the radiation is coherently scattered by the electrons in the atoms of the crystal.(14) In accordance with

electromagnetic theory, the amplitude of the wave scattered by the electron distribution $\rho(\bar{r})$ relative to the scattering by a single electron is

$$F(\bar{K}) = \int \exp(i\ \bar{K}\cdot\bar{r})\ \rho(\bar{r})\ d\bar{r} \qquad (1)$$

where $\bar{K}$ is the wave vector. (The derivation of this equation(15) can be found in Appendix A.) This Fourier transform relationship connecting the scattering factor $F(\bar{K})$ to the electron density $\rho(\bar{r})$ is a fundamental equation in crystallography.

The x-ray experiment measures the intensity, $I(\bar{K})$, of the scattered wave which is proportional to the square of the amplitude, $|F(\bar{K})|^2$. The experimentally measured intensity has to be corrected for effects such as x-ray absorption by the crystal, geometric factors that include polarization, temperature effect associated with the vibration of the nuclei, and other minor effects.(16) These experimental factors, however, can be modeled within known magnitudes of error, and the experiment gives structure factors, $F(\bar{K})$, related to the electron density, $\rho(\bar{r})$, characteristic of the crystal.

A connection between Crystallography and Quantum Mechanics is implicit in equation (1). This connection can be made apparent by ensuring that the structure factors come from an electron density consistent with the

restrictions of Quantum Mechanics; that is, only densities which are obtainable from the square of an antisymmetric wavefunction may be considered appropriate. Based on this idea, a density explicitly related to a set of molecular orbitals, ϕ_i, has been obtained by expanding the orbitals on a set of orthonormal basis functions, ψ_i, by the usual linear combination of atomic orbitals (LCAO) scheme, and the use of density matrices.

Given an antisymmetric N-body wavefunction, $\Psi(1...N)$, the one-body reduced density matrix, $\rho_1(1,1')$, is obtained by averaging the square of the wavefunction over all the spatial and spin coordinates, except for the coordinates of one particle(17-19)

$$\rho_1(1,1') = N\int \Psi^*(1,...N)\,\Psi(1',...N)\; d2...N \qquad (2)$$

The diagonal element of the first-order density matrix represents the electron density

$$\rho_1(1,1')\Big|_{1'\to 1} = \rho(1) \qquad (3)$$

In the particular case of a wavefunction which is a single determinant of orthonormal orbitals, i.e.,

$$\Psi(1,\ldots N) = \begin{vmatrix} \phi_1(1) & \cdots & \phi_1(N) \\ \vdots & & \\ \phi_N(1) & \cdots & \phi_N(N) \end{vmatrix} \tag{4}$$

the first-order density matrix, in a convenient matrix notation, is

$$\rho_1(\bar{r},\bar{r}') = \mathrm{tr}\ \underset{\sim}{\phi}(\bar{r})\ \underset{\sim}{\phi}^{+}(\bar{r}') \tag{5}$$

The expansion of the orbitals according to

$$\underset{\sim}{\phi}(\bar{r}) = \underset{\sim}{C}\ \underset{\sim}{\psi}(\bar{r}), \tag{6}$$

where the rectangular matrix $\underset{\sim}{C}$ contains the coefficients that combine the basis functions in the molecular orbitals, can be used in equation (5) to give

$$\rho_1(\bar{r},\bar{r}') = \mathrm{tr}\ \underset{\sim}{C}^{+}\ \underset{\sim}{C}\ \underset{\sim}{\psi}(\bar{r})\ \underset{\sim}{\psi}^{+}(\bar{r}') \tag{7}$$

The population matrix $\underset{\sim}{P}$ is defined as

$$\underset{\sim}{P} \equiv \underset{\sim}{C}^{+}\underset{\sim}{C} \tag{8}$$

With this definition, equation (7) becomes

$$\rho_1(\bar{r},\bar{r}') = \mathrm{tr}\ \underset{\sim}{P}\ \underset{\sim}{\Psi}(\bar{r})\ \underset{\sim}{\Psi}^{+}(\bar{r}') \tag{9}$$

whose diagonal element

$$\rho_1(\bar{r}) = \mathrm{tr}\ \underset{\sim}{P}\ \underset{\sim}{\Psi}(\bar{r})\ \underset{\sim}{\Psi}^{+}(\bar{r}) \tag{10}$$

can be used in the Fourier transform relationship for the structure factor to get

$$F(\bar{K}) = \mathrm{tr}\ \underset{\sim}{P}\ \underset{\sim}{f}(\bar{K}) \tag{11}$$

where the matrix $\underset{\sim}{f}(\bar{K})$ has as elements, $f_{ij}(\bar{K})$, Fourier transforms of basis functions products,

$$f_{ij}(\bar{K}) \equiv \int \exp(i\ \bar{K}\cdot\bar{r})\ \Psi_i(\bar{r})\ \Psi_j^{*}(\bar{r})\ d\bar{r} \tag{12}$$

From equation (11) follows that the elements of $\underset{\sim}{P}$ can be treated as parameters to be fit to the experimental structure factors, $F(\bar{K})$. It must be noted, however, that any simple fitting procedure of the elements of $\underset{\sim}{P}$ to the experimental data does not necessarily lead to density

matrices which are quantum mechanically valid. This is the problem of N-representability, which can be explained as a mapping problem.

Given the set of all antisymmetric N-body wavefunctions, $\Psi(1...N)$, the set of all valid one-body reduced density matrices, $\rho_1(\bar{r},\bar{r}')$, is obtained by following the prescription of equation (2). However, the set of all possible one-body functions is larger than the set of $\rho_1(\bar{r},\bar{r}')$, and consequently it is not any one-body function that can be mapped back to an N-body wavefunction. A simple fitting procedure such as the least-squares method will almost always yield a density matrix that is not related to a N-body wavefunction by the rule of equation (2), meaning that the quantum mechanical restrictions must be imposed in addition to fitting procedures.

The problem of N-representability of the one-body density matrix has been solved. It has been shown(20) that N-representability is guaranteed by the requirement that the eigenvalue, which has the physical interpretation of occupation numbers of molecular orbitals, be a number between zero and one, i.e.,

$$\int \rho_1(\bar{r},\bar{r}')\ \phi_i(\bar{r}')\ d\bar{r}' = \varepsilon_i\ \phi_i \qquad (13)$$

with

$$0 \leq \varepsilon_i \leq 1 \tag{14}$$

In particular, the values 0 and 1 are necessary and sufficient for $\rho_1(\bar{r},\bar{r}')$ to be N-representable by a single determinant(18) of orbitals of the type of equation (4). Furthermore, Gilbert's theorem(21) states that any non-negative density which is normalized to the number of electrons, N, is N-representable by a single-determinant wavefunction, and Harriman(22) has given a construction to get such a determinant from the density. It is then natural to found a formalism on single determinant N-representability of $\rho_1(\bar{r},\bar{r}')$.

The condition stated in equation (13) and (14) is equivalent to the requirement that $\rho_1(\bar{r},\bar{r}')$ be idempotent or a projector

$$\rho_1(\bar{r}',\bar{r}'')\ \rho_1(\bar{r}'',\bar{r})\ d\bar{r}'' = \rho_1(\bar{r}',\bar{r}) \tag{15}$$

Finally, hermiticity

$$\rho_1(\bar{r}',\bar{r}) = \rho_1^{*}(\bar{r},\bar{r}') \tag{16}$$

and normalization to the total number of electrons

$$\varrho_1(\bar{r},\bar{r})\ d\bar{r} = N \tag{17}$$

are known to be satisfied by a single determinant of orthonormal orbitals.(17,18) Since a matrix representative $\underset{\sim}{P}$ in any basis must have the same properties it follows that the population matrix $\underset{\sim}{P}$ must be a symmetric normalized projector, and has to satisfy the experimental structure factors, i.e.,

$$\begin{aligned} &\underset{\sim}{P} = \underset{\sim}{P}^{+} && \text{(a)} \\ &\text{tr}\ \underset{\sim}{P} = N && \text{(b)} \\ &\underset{\sim}{P}^2 = \underset{\sim}{P} && \text{(c)} \\ &\text{tr}\ \underset{\sim}{P}\ \underset{\sim}{f}(\bar{K}) = F(\bar{K}) && \text{(d)} \end{aligned} \tag{18}$$

These four equations are the mathematical structure that brings Quantum Mechanics in contact with the crystallographic experiment. $\underset{\sim}{P}$ matrices which conform to the conditions established by equations (18) may be obtained as solutions of Clinton's equations(23), in the iterative form,

$$\underset{\sim}{P}_{n+1} = 3\,\underset{\sim}{P}_n^2 - 2\,\underset{\sim}{P}_n^3 + \lambda_K\,\underset{\sim}{f}(K) + \lambda_N\,\underset{\sim}{1} \qquad (19)$$

where λ_K and λ_N are Lagrangian multipliers determined by constraints satisfying structure factors and normalization. Importantly, the proper fundamental constraints in Clinton's equations not only allow for physically meaningful model wavefunctions but also reduce the number and correlation of parameters within the population matrix.(4,5,7)

The quantum description of the x-ray scattering experiment incorporated in Clinton's equations has been applied to a number of physical systems. The studies include simple theoretical models such as H, H_2, Li, and Be, and real experimental data of high accuracy for the beryllium crystal.

In the case of the atoms and H_2 the structure factors are generated mathematically from wavefunctions or densities assumed to be exact. The data, therefore, contain no errors due to absorption or extinction of x-rays, nor do they contain any thermal motion effects. Consequently, the results represent a test of the mathematical structure associated with N-representability.

Frishberg and Massa(11) have used the structure factors of Stewart, Davidson and Simpson(24) for a spherical hydrogen atom in a hydrogen molecule as constraints in the determination of the idempotent $\underset{\sim}{P}$

matrix. They also carried out a conventional least-squares analysis where idempotency was not imposed. A good fit was obtained in both cases, although it was slightly better for the non-idempotent case.

From their results we learn that the density matrix is everywhere positive as it is expected to be for a quantity interpreted as a probability distribution. The non-idempotent density matrix becomes negative near the nucleus, a result which is physically meaningless. The eigenvalues of the idempotent density matrix are 0 and 1, in accord with Coleman's theorem(20). The non-idempotent density matrix has eigenvalues that fall outside the allowable interval and thus violate the Pauli principle.

The application of the x-ray orbitals formalism to bonding effects was also investigated by Frishberg and Massa.(11) They considered the H_2 molecular density of Stewart, Davidson and Simpson(24), and solved the equations (18) with different sets of basis functions. Their results reproduce the known charge distribution and bond distance of the molecule. More recently, Boehme and La Placa(13) have obtained an empirical wavefunction for molecular hydrogen by solving equations (18) and using the x-ray scattering data of Stewart, Davidson and Simpson(24) for the hydrogen molecule. Their wavefunction is capable of giving a very low crystallographic R factor, and of predicting physical properties very accurately. The

calculated bond energy is almost as good as the one obtainable with the same basis in an energy minimization.

Lithium and beryllium atoms have been studied by Frishberg and Massa.(10) They used the essentially exact structure factors calculated by Benesch and Smith(25,26) as the data for the solution of equation (18). Structure factors were calculated with the x-ray orbitals and the Hartree-Fock orbitals, the same basis in either case. The fit to the exact structure factors is much better when x-ray orbitals are used. This is an interesting finding since the Hartree-Fock wavefunction is considered to yield an accurate density.

A number of properties were calculated for lithium and beryllium using essentially exact wavefunctions, and Hartree-Fock and x-ray wavefunctions on the same basis. The results are shown in table 1. In both cases the x-ray orbitals yield total energies very close to the Hartree-Fock energies, in fact within 0.010 per cent. Of course, by definition, the Hartree-Fock energies must be lower than in the x-ray case. The expectation values for the one-electron properties such as $\langle -\frac{1}{2}\nabla^2 \rangle$ and $\langle 1/r \rangle$, are all better calculated by the x-ray wavefunction than by the Hartree-Fock wavefunction for both atoms. The electron-electron repulsion term, $\langle 1/r_{12} \rangle$, is slightly better evaluated by the Hartree-Fock function.

Table 1. Some expectation values from the exact, Hartree-Fock, and x-ray orbitals single-determinant for the lithium and beryllium atoms. Adapted from Ref. (10)

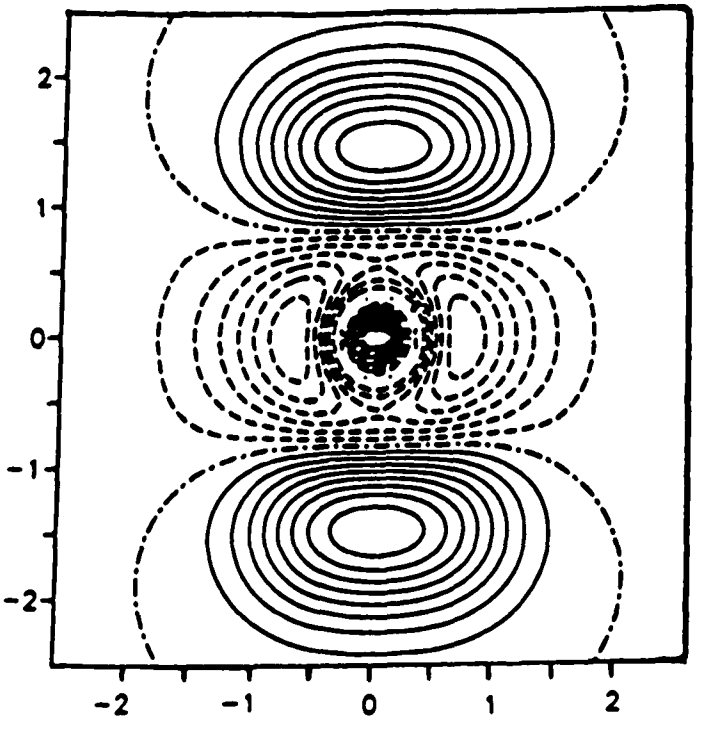
		Total energy	Kinetic energy	$\langle \frac{1}{r_{12}} \rangle$	$\langle \frac{1}{r} \rangle$	$\langle r^2 \rangle$
Li	Exact	-7.478025	7.478	2.199	5.71822	18.35034
	HF	-7.432749	7.433	2.281	5.71549	18.62610
	XR	-7.432694	7.438	2.285	5.71866	18.34609
Be	Exact	-14.66090	14.66	4.3803	8.4246	
	HF	-14.57302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

The x-ray orthonormal orbital model has also been applied to obtain the wavefunction characteristic of the full crystal of beryllium metal. Massa, Goldberg, Frishberg, Boehme and La Placa(12) used the very accurate experimental data of Hansen and Larsen(27) to obtain a wavefunction for beryllium hybrid-atomic fragments, which placed at their lattice positions yield the exact electron density of the crystal.

The effect of crystal bonding on the atomic fragments are mainly reflected in the valence density. To show the non-spherical features accounted for by the x-ray orbital model we reproduce two pictures of the valence density. Figure 1 is a deformation density, obtained as the

difference of the full electron density calculated with the x-ray valence orbital less the electron density of a free spherical atom. A build up of charge takes place along the c-axis, which in this picture lies along the vertical direction. This result correlates well with the crystal's compression along the c-axis.

Figure 1. Model deformation density for the hybrid Be atom. Contour interval is 0.01 (e/A^3). Positive contours, solid; zero, dot-dashed; negative, dashed. Massa et al. (1985), Ref. (12)

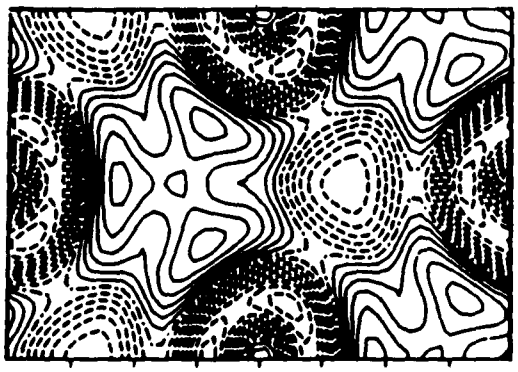


Below, figure 2 shows a comparison of the x-ray valence density with two of the best available theoretical calculations(28,29), in a cut through an a-b horizontal plane of the crystal. The concordance is excellent. There is an accumulation of electron density in the tetrahedral

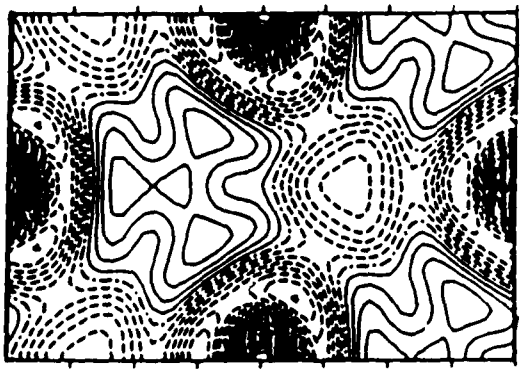
holes compensated by a depletion of electron density in the octahedral holes of the crystal.

Figure 2. Valence density from (a) Dovesi et al., (b) Massa et al., and (c) Chou et al. Contour intervals are as in Figure 1 except that the zero contour refers to four electrons per unit cell volume. From Ref. (12)

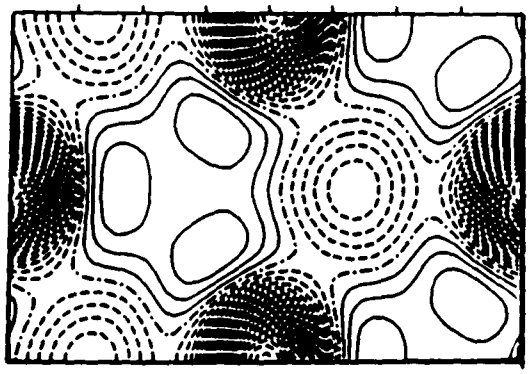
(a)



(b)



(c)



The crystallographic R-factor is a very small value (0.0018) indicating a very good fit of the model to the experimental data. Additionally, the errors in the calculated structure factors are in close accordance with a normal distribution of errors.

After having summarized the studies carried out with the x-ray orbital model of crystallography, a number of points regarding the application of the formalism can be emphasized. First, the importance of obtaining idempotent density matrices in order to get physically meaningful results has been demonstrated.(2-12) Second, in every system studied the relevant features of the charge distribution are reproduced.(2-12) Third, density-dependent properties are accurately predicted.(10,12,13) Fourth, and this is probably the most relevant point, the present method of analysis of the x-ray data obtains orbitals, while other methods do not. Hence, momentum dependent properties such as the kinetic energy can also be calculated.(30,31)

We now turn our attention to the correlation problem, which by definition is neglected in the single-determinant approximation.

More than fifty years ago, Wigner(32) introduced as a measure of correlation the correlation energy defined as

$$E_c = E_{exact} - E^{HF} \qquad (20)$$

where E^{HF} is the Hartree-Fock energy, and E_{exact} is the eigenvalue of the non-relativistic Hamiltonian.

The notion that electrons which repel each other are less likely to be found close together than in the absence of interaction can be made quantitative in terms of probabilities. The probability per unit volume of finding one electron at point $\bar{r}_1$ is given by the diagonal element of the one-body density matrix $P_1(\bar{r}_1)$, and that of finding any two electrons simultaneously at points $\bar{r}_1$ and $\bar{r}_2$ is given by the diagonal element of the two-body density matrix, $P_2(\bar{r}_1,\bar{r}_2)$.

If the electrons were non-interacting particles, the multiplicative law for the simultaneous occurrence of independent events would give

$$P_2(\bar{r}_1,\bar{r}_2) = P_1(\bar{r}_1)\cdot P_1(\bar{r}_2) \qquad (21)$$

However, equation (21) does not describe the physical situation, and a term accounting for the lack of independence of the electrons should be added. It is convenient to introduce a "correlation factor"(17) such that

$$P_2(\bar{r}_1,\bar{r}_2) = P_1(\bar{r}_1)\cdot P_1(\bar{r}_2)\cdot(1+f(\bar{r}_1,\bar{r}_2)) \qquad (22)$$

According to probability theory, the conditional probability of finding an electron at point $\bar{r}_1$ when another electron is at point $\bar{r}_2$ is given by the quotient $P_2(\bar{r}_1,\bar{r}_2)/P_1(\bar{r}_2)$. Then, using equation (22), we have

$$\frac{P_2(\bar{r}_1,\bar{r}_2)}{P_1(\bar{r}_2)} = P_1(\bar{r}_1)\cdot(1+f(\bar{r}_1,\bar{r}_2)) \qquad (23)$$

which, due to electron-electron repulsion, is expected to be smaller than $P_1(\bar{r}_1)$.

For point $\bar{r}_1$ approaching point $\bar{r}_2$ the correlation factor is negative, and therefore makes a "hole" in the one-particle probability surrounding any point at which there is already a particle. McWeeny uses the function(33,34)

$$F_{r_2}(\bar{r}_1) = P_1(\bar{r}_1)\cdot f(\bar{r}_1,\bar{r}_2) \qquad (24)$$

to describe the correlation hole around a reference electron at position $\bar{r}_2$. To study the correlation hole it is convenient to express the spinless density matrices as a sum of terms each associated with a spin configuration, in particular the diagonal elements are

$$P_1(\bar{r}_1) = P_1^{\alpha}(\bar{r}_1)+P_1^{\beta}(\bar{r}_1) \tag{25}$$

where $P_1^{\alpha}(\bar{r}_1)$ is the probability per unit volume of finding an electron at point $\bar{r}_1$ in spin state α, and $P_1^{\beta}(\bar{r}_1)$ is the probability per unit volume of finding an electron at point $\bar{r}_1$ in spin state β.

Similarly,

$$P_2(\bar{r}_1,\bar{r}_2) = P_2^{\alpha\alpha}(\bar{r}_1,\bar{r}_2)+P_2^{\alpha\beta}(\bar{r}_1,\bar{r}_2)+P_2^{\beta\alpha}(\bar{r}_1,\bar{r}_2)+P_2^{\beta\beta}(\bar{r}_1,\bar{r}_2) \tag{26}$$

where $P_2^{\alpha\alpha}(\bar{r}_1,\bar{r}_2)$ is the probability per unit volume of finding an electron at point $\bar{r}_1$ in spin state α while another one is at point $\bar{r}_2$ in spin state α ; $P_2^{\alpha\beta}(\bar{r}_1,\bar{r}_2)$ is the probability per unit volume of finding an electron at point $\bar{r}_1$ in spin state α while another one is at point $\bar{r}_2$ in spin state β, and so forth.

Using the correlation factor introduced in equation (22), we have

$$P_2^{\alpha\alpha}(\bar{r}_1,\bar{r}_2) = P_1^{\alpha}(\bar{r}_1)\cdot P_1^{\alpha}(\bar{r}_2)\cdot(1+f^{\alpha\alpha}(\bar{r}_1,\bar{r}_2)) \tag{27}$$

and

$$P_2^{\alpha\beta}(\bar{r}_1,\bar{r}_2) = P_1^{\alpha}(\bar{r}_1)\cdot P_1^{\beta}(\bar{r}_2)\cdot(1+f^{\alpha\beta}(\bar{r}_1,\bar{r}_2)) \tag{28}$$

The antisymmetry of the wavefunction is inherited by the density matrices, therefore $P_2^{\alpha\alpha}(\bar{r}_1,\bar{r}_2)$ must go to zero when $\bar{r}_1$ tends to $\bar{r}_2$, and consequently $f^{\alpha\alpha}(\bar{r}_1,\bar{r}_2)$ and $f^{\beta\beta}(\bar{r}_1,\bar{r}_2)$ tend to -1. In other words, there is zero probability of finding electrons with the same spin at the same point in space which is in harmony with the Pauli principle.

The correlation between electrons arising from the antisymmetry of the wavefunction is usually referred to as the "Fermi correlation". For unlike spins there are no restrictions on $P_2^{\alpha\beta}(\bar{r}_1,\bar{r}_2)$, however electrons of opposite spins are kept from being too close to one another by electrostatic repulsion. This effect is called "Coulomb correlation".(33)

We consider now a wavefunction which is a single-Slater determinant. The two-body density matrix can be written in terms of one-body density matrices

$$\rho_2(\bar{x}_1,\bar{x}_2;\bar{x}_1',\bar{x}_2') = \rho_1(\bar{x}_1,\bar{x}_1')\,\rho_1(\bar{x}_2,\bar{x}_2') - \rho_1(\bar{x}_1,\bar{x}_2')\,\rho_1(\bar{x}_2,\bar{x}_1') \qquad (29)$$

Then, after integrating over the spin coordinates we have

$$P_2^{\alpha\alpha}(\bar{r}_1,\bar{r}_2) = P_1^{\alpha}(\bar{r}_1)\cdot P_1^{\alpha}(\bar{r}_2) - P_1^{\alpha\alpha}(\bar{r}_1,\bar{r}_2)\cdot P_1^{\alpha\alpha}(\bar{r}_2,\bar{r}_1) \qquad (30)$$

$$P_2^{\beta\beta}(\bar{r}_1,\bar{r}_2) = P_1^{\beta}(\bar{r}_1)\cdot P_1^{\beta}(\bar{r}_2) - P_1^{\beta\beta}(\bar{r}_1,\bar{r}_2)\cdot P_1^{\beta\beta}(\bar{r}_2,\bar{r}_1) \quad (31)$$

$$P_2^{\alpha\beta}(\bar{r}_1,\bar{r}_2) = P_1^{\alpha}(\bar{r}_1)\cdot P_1^{\beta}(\bar{r}_2) \quad (32)$$

$$P_2^{\beta\alpha}(\bar{r}_1,\bar{r}_2) = P_1^{\beta}(\bar{r}_1)\cdot P_1^{\alpha}(\bar{r}_2) \quad (33)$$

Equations (30) to (33) show that for electrons of the same spin $P_2(\bar{r}_1,\bar{r}_2)$ contains a correlation term, whereas for electrons of opposite spin correlation is absent. Thus, a single-determinant wavefunction accounts for Fermi correlation but fails to describe Coulomb correlation.

Most of the quantum mechanical calculations on many-electron systems are carried out by the self-consistent-field approximation (SCF), which disregards correlation. Hence, methods of evaluation of the correlation energy are very important in order to correct the results of ab initio Hartree-Fock calculations.

Following McWeeny(34), we group the methods of calculation of the correlation energy in basically two

types, those which involve configuration interaction (CI), and those which involve the correlation factor.

Usually, CI methods are concerned with the implementation in a variational way of a so-called cluster development of the wavefunction (35,36). An infinite CI expansion of the general form

$$\Psi = c_o \Phi_o + \sum_{i,m} c_i^m \Phi_i^m + \sum_{\substack{i<j \\ m<n}} c_{ij}^{mn} \Phi_{ij}^{mn} + \ldots \qquad (34)$$

is obtained with an orthonormal set of occupied orbitals, ($\psi_i=\psi_1 \ldots \psi_N$), and an orthonormal set of virtual orbitals ($\psi_m=\psi_{N+1} \ldots \psi_m \ldots$). The leading term contains occupied spin orbitals and may be taken as the Hartree-Fock determinant. The other terms are single "excitations" ($i \rightarrow m$), double "excitations" ($i,j \rightarrow m,n$), etc.

A common method in CI calculations is to include all single and double excitations to get a limited CI expansion.

The cluster development is obtained by factoring out the N-electron antisymmetrizer, $A = (N!)^{-1} \sum (-1)^p P$, in the determinants of equation (34)

$$\Psi = \sqrt{N!}\ A\ (\varphi_o \Omega_o + \sum_i \varphi(x_i) \Omega_i(x_1, \ldots x_N) +$$

$$\frac{1}{\sqrt{2}} \sum_{i<j} \varphi_{ij}(x_i, x_j) \Omega_{ij}(x_1, \ldots x_N) + \ldots) \qquad (35)$$

where Ω_o is the orbital product in the Hartree-Fock determinant and Ω_{ij}, for instance, is the product Ω_o with Ψ_i and Ψ_j removed. The space-spin variable is denoted by x_i.

The functions φ_o, $\varphi_i(x_i)$, $\varphi_{ij}(x_i,x_j)$... have the form

$$\varphi_o = c_o$$

$$\varphi_i(x_i) = \sum_m c_i^m \Psi_m(x_i) \tag{36}$$

$$\varphi_{ij}(x_i,x_j) = \sum_{m<n} c_{ij}^{mn} \frac{1}{\sqrt{2}} \det \Psi_m(x_i)\, \Psi_n(x_j)$$

and they are referred to as one-cluster, two-cluster,... functions. The one-cluster function may be interpreted as a correction to the function Ψ_i, the two-cluster function as a correction to the product $\Psi_i \cdot \Psi_j$, and so forth. The general function φ_{ij} describes a "correlated pair".

In almost all calculations involving cluster developments, clusters for more than two particles are neglected. Although four-cluster functions may be important they are mainly describing antisymmetrized products of independent two-cluster functions and are said to be "unlinked".

The separation of linked and unlinked clusters is generally accomplished by second-quantization methods,(36) and the right choice of orbital basis allows for elimination of the one-cluster functions. The cluster development takes then the form

$$\Psi = \sqrt{N!}\ A\ (\varphi_o \Omega_o + \sum_{(ij)} \frac{1}{\sqrt{2}}\ \varphi_{ij}\ \Omega_{ij} + \sum_{(ij)}\sum_{(kl)} \frac{1}{\sqrt{2}}\ \varphi_{ij}\ \frac{1}{\sqrt{2}}\ \varphi_{kl}\ \Omega_{ijkl} + \dots\ ) \qquad (37)$$

where (ij) and (kl) are pairs with no common index, and three-cluster functions (and higher) have been neglected.

There are many approaches to the implementation of the equation above.(37-41) We will mention only two of them. The independent-electron-pair approximation (IEPA), first developed by Sinanoglu,(38-41) considers one correlated pair at a time. The coefficients, c_{ij}^{mn}, of a variation function

$$\Psi_{ij} = \Phi_o + \sum_{mn} c_{ij}^{mn}\ \Phi_{ij}^{mn} \qquad (38)$$

with Φ_o usually chosen as the single Hartree-Fock determinant, are optimized for every pair independently, and the energy E_{ij} associated with the function (38)

defines a pair correlation energy $\varepsilon_{ij} = E_{ij} - E^{HF}$. A first-order estimate of the correlation energy is then

$$Ec \cong \sum_{ij} \varepsilon_{ij} \tag{39}$$

This method is not rigorous in its decoupling of the pairs and their contributions to the correlation energy. Results violating the variational theorem are therefore not precluded. In the coupled electron-pair approximation (CEPA) developed by Meyer(42), equation (34) is written as

$$\Psi = C_o \Phi_o + \sum_{P,(mn)} C_P^{mn} \Phi_P^{mn} + \sum_M C_M \Phi_M \tag{40}$$

where P is a given pair and M is a "multiple pair excitation", and a system of secular equations is solved to determine the C_P^{mn} simultaneously for all pairs. In this way, highly accurate wavefunctions for small molecules have been obtained, but the simultaneous optimization of parameters corresponding to all the different pairs is of great technical difficulty.

Work has also been done in perturbation methods with the introduction of diagrammatic techniques to handle and sum the various types of terms in a perturbation expansion. Gell-Mann and Brueckner(43) have developed this method for

the free-electron gas, and Kelly(44) for atoms. Kelly's method is capable of delivering more than 90 per cent of the correlation energy for small atoms, but the extension of the method to molecules raises severe computational problems due to the normally slow convergence of the functions.

Finally, we discuss approximations based on the use of the correlation factor. It has been known for many years now, since the works of Hylleraas(45,46) and of James and Coolidge(47), that the use of interelectronic variables in a two-particle wavefunction can lead to solutions of high accuracy.

Pekeris'(48,49) helium atom calculations and Kolos and Wolniewicz's(50) hydrogen molecule calculations well illustrate this point. But generalization to many-electron systems has met unsurmountable difficulties.(34)

Nevertheless, approximation methods have been developed to simplify the scheme and make it mathematically tractable. We consider two such approaches which are similar to the way we will deal with the problem; the method of Boys and Handy and methods based on the correlation hole.

Boys(51) proposed new methods of using a correlated wavefunction of the form

$$\Psi = c\,\Phi_0 \qquad (41)$$

where the factor C is a symmetric function containing the interelectronic variables

$$C = \prod_{i<j} F(\bar{r}_i, \bar{r}_j) \tag{42}$$

and Φ_o may be a single Slater determinant. Since the correlation function depends also on the electron density both vectors $\bar{r}_i$ and $\bar{r}_j$ are to be included in the function or, alternatively

$$\bar{R}_{ij} = \frac{1}{2}(\bar{r}_i + \bar{r}_j) \quad , \quad \bar{r}_{ij} = \bar{r}_i - \bar{r}_j \tag{43}$$

The form of the function in equation (40) makes the variational energy expression intractable, and therefore Boys and Handy(52,53) suggested a modified variational procedure

$$\langle \delta\Psi^+ | (H-E) | \Psi \rangle = 0 \tag{44}$$

where

$$\Psi^+ = C^{-1} \Phi_o \tag{45}$$

For arbitrary variations, the quantity in equation (44) still vanishes only when $H\Psi = E\Psi$, so that in this way it is insensitive to the specific correlation factor used.

The functional

$$\langle\Phi_o|C^{-1}\ H\ C|\Phi_o\rangle \qquad (46)$$

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

The use of suitable forms of $F(\bar{r}_i,\bar{r}_j)$ has yielded very accurate wavefunctions and consequently highly accurate estimates of the energy when applied to the neon atom(54) and the molecule LiH.(55) But many difficulties arise when the method is applied to larger systems.(34)

Methods based on the correlation hole are those which estimate the correlation energy by using some analytical form of the correlation hole within the framework of the Hartree-Fock calculation. Colle and Salvetti(56) have worked on these lines and obtained an empirical formula for the calculation of the correlation energy from knowledge of the Hartree-Fock two-body density matrix. We will discuss this work in detail in Chapter 2.

The calculation of the correlation energy is an important problem, as R. McWeeny has indicated:

> ..."important work on electron correlation is in progress and until it has reached fruition,..., 'chemical accuracy' for systems of moderate size will not be achieved." (34)

Furthermore, evaluation of correlation effects is a very difficult and complex task. Most of the calculations of correlation energy are performed by CI methods which require the solution of extensive systems of secular equations demanding an enormous amount of computational work.

In the present study the correlation problem is addressed by using methods based on the correlation hole. One of the advantages following from this choice of approach is the great reduction of computational work that it brings about.

We investigate the method of Colle and Salvetti and obtain numerical results for the correlation energy with their formula for the series of ions isoelectronic with helium and the series of ions isoelectronic with beryllium.

We develop a formalism for the calculation of the correlation energy by a method based on the correlation hole within the framework of the x-ray orthonormal orbital model. And, we perform test calculations on helium, beryllium, and a series of ions isoelectronic with each of them.

CHAPTER 2 THE COLLE-SALVETTI FORMALISM FOR THE CORRELATION ENERGY

1. The Colle-Salvetti Formula

Colle and Salvetti have developed a method for the approximate calculation of correlation energy starting from knowledge of the Hartree-Fock determinant of the system.(56-63)

They approximate the N-body wavefunction by

$$\Psi(1,\ldots N) = \Psi^{HF}(1,\ldots N) \prod_{i<j} (1-\varphi(\bar{r}_i,\bar{r}_j)) \qquad (47)$$

where $\Psi^{HF}(1,2,\ldots,N)$ is the Hartree-Fock wavefunction, and the spinless function $\varphi(\bar{r}_i,\bar{r}_j)$, which brings in the correlation effects, is to be determined. The form of $\varphi(\bar{r}_i,\bar{r}_j)$ is chosen to be

$$\varphi(\bar{r}_i,\bar{r}_j) = \exp(-\beta^2 r^2)\ (1-\bar{\Phi}(\bar{R})\ (1+r/2)) \qquad (48)$$

where

$$r = |\bar{r}_i-\bar{r}_j| \quad ; \quad \bar{R} = \tfrac{1}{2}(\bar{r}_i+\bar{r}_j) \qquad (49)$$

With this functional form for $\varphi(\bar{r}_i,\bar{r}_j)$ the wavefunction satisfies the cusp conditions for $\bar{r}_1 \rightarrow \bar{r}_2$,(64) and becomes a Hartree-Fock determinant when the electrons are far apart.

The notion that the volume in which $\varphi(\bar{r}_i,\bar{r}_j)$ is significant is proportional to the exclusion volume of Wigner(65) yields

$$4\pi \int_0^\infty \exp(-\beta^2 r^2)\ r^2\ dr \propto \rho^{-1} \tag{50}$$

where ρ is the electron density.

By evaluating the integral in equation (50) and introducing a proportionality constant one has

$$\beta = q\ \rho^{\frac{1}{3}} \tag{51}$$

The spinless second-order density matrix, obtained by the usual rules,(17,18) is approximated by

$$P_2(121'2') = P_2^{HF}(121'2')\ ((1-\varphi(12))\ (1-\varphi(1'2'))) \tag{52}$$

Making the assumption that the Hartree-Fock first-order density matrix approximates well enough the first-order

density matrix obtained by integration of the exact $P_2(121'2)$, i.e.,

$$P_1(11') = P_1^{HF}(11') \quad , \tag{53}$$

it follows

$$\int P_2^{HF}(121'2)\ (\varphi(12)\ \varphi(1'2) - \varphi(12) - \varphi(1'2))\ d\bar{r}_2 = 0 \tag{54}$$

from which a functional form for Φ is derived

$$\Phi(\bar{R}) = \frac{\sqrt{\pi}\ \beta(\bar{R})}{1 + \sqrt{\pi}\ \beta(\bar{R})} \tag{55}$$

Within this framework the total energy, E, is

$$E = E^{HF} + \frac{1}{2}\int P_2^{HF}(1212)\ \frac{(\varphi^2(12) - 2\ \varphi(12))}{r}\ d\bar{r}_1\ d\bar{r}_2 \tag{56}$$

where E^{HF} is the Hartree-Fock energy, and the second term on the right-hand side of the equation is the correlation energy, Ec.

The method does not require the evaluation of the double integral in equation (56). Instead, an empirical

formula involving integration over $\bar{R}$ only is proposed by the authors

$$E_c = -0.04918 \int \rho(\bar{R}) \frac{1+0.173\ W \exp(-0.58/\beta)}{1+0.8/\beta} d\bar{R} \qquad (57)$$

with $\beta(\bar{R}) = 2.29\ \rho^{\frac{1}{3}}(\bar{R})$ and

$$W = 0.3814\ \rho^{-\frac{8}{3}}(\bar{R})\ \left(\nabla_r^2\ P_2^{HF}(\bar{R}-\frac{\bar{r}}{2}, \bar{R}+\frac{\bar{r}}{2}) \right)_{\bar{r}=0}$$

All the coefficients in equation (57) were chosen so as to give the correlation energy of helium.

A number of ground-state systems have been studied using this formula and excellent results have been obtained.(56) Examples are listed in table 2.

Table 2. Correlation energy for some atoms and small molecules calculated by Colle and Salvetti compared to the values calculated by Clementi. From Ref. (56)

	Ec (a.u.) Colle-Salvetti	Ec (a.u.) Ref.(68,74)	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
		-0.340	1.2

Correlation contribution to excitation energies, ionization potentials and dissociation energies for some small atoms and molecules have been successfully calculated by employing the Colle-Salvetti formula.(57-59) Such results are presented in table 3.

Table 3. Excitation energies, ionization potentials and dissociation energies calculated by adding to the HF or MC-SCF values of the correlation contribution given by equation (57), compared to the exact values. From Ref. (63)

System			ΔE (eV) (CS-formula)	ΔE (eV) (exact)
Be	^1S	$(2s \rightarrow 3s)$	6.7	6.8
	^1S	$(2s \rightarrow 4s)$	8.1	8.1
C_2H_4	$^1B_1$	$(1b_1 \rightarrow 1b_2)$	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
	$^2B_1$	ionization potential	10.65	10.88
H_2	$X^1\Sigma^+$	dissociation energy	4.72	4.75

The functional has also been applied to the calculation of the correlation energy of the electron gas,(34) reproducing the high and low density results of Gell-Man and Brueckner(43) and of Carr(66). Additionally, the formula allows for calculation of the correlation energy in the region of intermediate densities, where the methods of Gell-Mann and Brueckner, Pines and others are not convergent.

These numerical results show that the Colle-Salvetti formula is a very interesting alternative to the time consuming CI calculations. Moreover, it is easy to implement and yields excellent results. In fact, the highest error reported is eight per cent of the correlation energy.

2. The Exact-density Determinant and the Colle-Salvetti Formula

Cohen et al.(67) have used the formula of Colle and Salvetti to calculate the correlation energy substituting the HF determinant with the determinant of x-ray orbitals, which delivers the exact density. The second-order density matrix is now

$$P_2(121'2') = P_{2\underline{det}}(121'2')\ ((1-\varphi(12))\ (1-\varphi(1'2'))) \qquad (58)$$

where the subscript det means determinant delivering the exact density.

For the first-order density matrix Colle and Salvetti have assumed that it is well approximated by the Hartree-Fock one-body density matrix. Cohen et al. have assumed that the one-body density matrix delivering the exact

density is also a good approximation to the exact first-order density matrix. The assumption is based on the fact that several one- and two-body properties for atoms calculated with the exact density determinant are comparable in accuracy to those calculated with the Hartree-Fock determinant. And indeed, nothing prevents both the two determinants from giving good approximations to the exact one-body density matrix.

The derivation of $\bar{\Phi}(\bar{R})$ requires equation (53) to hold only for the diagonal element. Hence, for the exact density determinant case, this is a true equation.

The correlation energy of the beryllium atom was the test calculation performed by the authors. They evaluated equation (57) using the exact density determinant instead of the Hartree-Fock one. They obtained Ec = -0.093618 a.u., that added to the energy of the exact density determinant (see table 1) yields a total energy E = -14.665068 a.u. When the Hartree-Fock energy (see table 1) is subtracted from this quantity the correlation energy obtained Ec = -0.092054 a.u., differs by less than two per cent from the value calculated by Veillard and Clementi(68), (-0.0940 a.u.), and by less than one per cent from the result of Colle and Salvetti (see table 2). It is worth noting that in this study the determinant of x-ray orbitals was used for the first time to calculate the correlation energy, and this first numerical experiment has yielded an excellent result.

3. Calculation of the Correlation Energy for Two Series of Isoelectronic Ions

The impressive results obtained with the Colle-Salvetti formula for several systems, within the Hartree-Fock scheme and within the x-ray orbitals scheme (for one case so far), motivated a further investigation of its applications.

Calculations of the correlation energy were carried out for the series of ions isoelectronic with helium and the series of ions isoelectronic with beryllium, using the Hartree-Fock functions computed by E. Clementi.(69) The integral of equation (57) was evaluated numerically by using the trapezoidal rule(70). The analytical form for W as well as the necessary operators are collected in Appendix B.

The results are displayed in figure 3 and table 4 for the helium-like ions, and in figure 4 and table 5 for the beryllium-like ions.

Figure 3. Correlation energy for the series of ions isoelectronic with helium.

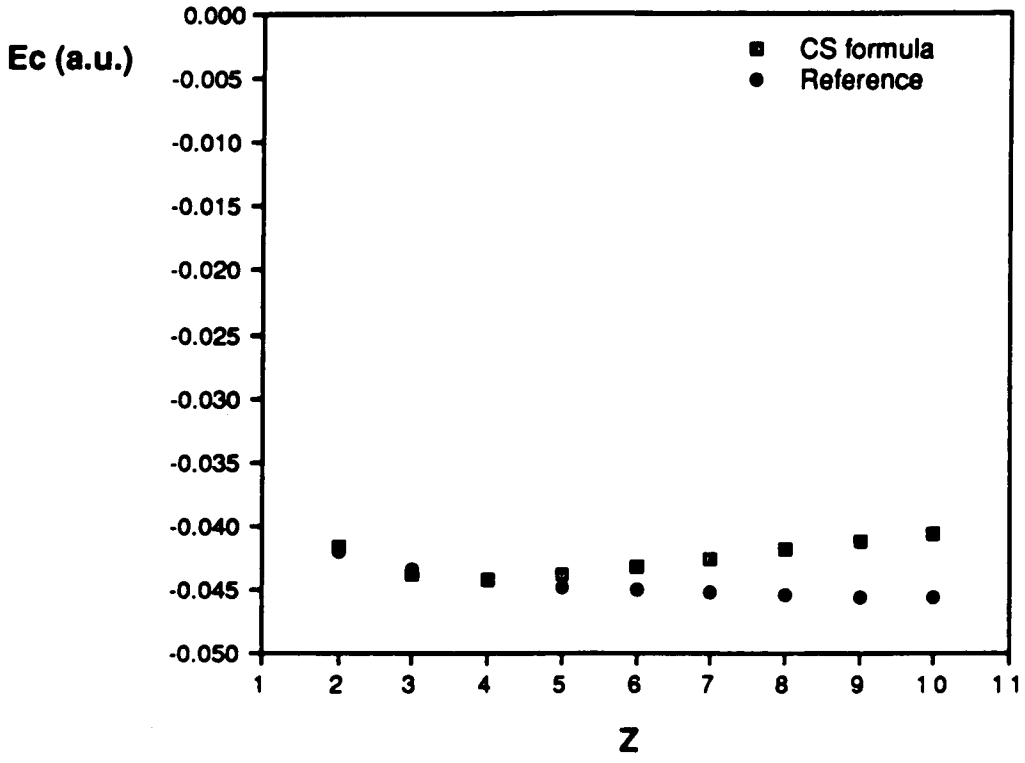


Table 4. Correlation energy for the series of ions isoelectronic with helium.

	Z	Ec (a.u.) CS-formula	Ec (a.u.) Ref.(68,74)	Error (%)
He	2	-0.0416	-0.0420	1.0
Li^{+}	3	-0.0439	-0.0435	0.9
Be^{2+}	4	-0.0442	-0.0443	0.2
B^{3+}	5	-0.0439	-0.0448	2.1
C^{4+}	6	-0.0433	-0.0451	4.0
N^{5+}	7	-0.0426	-0.0453	5.9
O^{6+}	8	-0.0419	-0.0455	7.8
F^{7+}	9	-0.0413	-0.0456	9.5
Ne^{8+}	10	-0.0406	-0.0457	11.1

Figure 4. Correlation energy for the series of ions isoelectronic with beryllium.

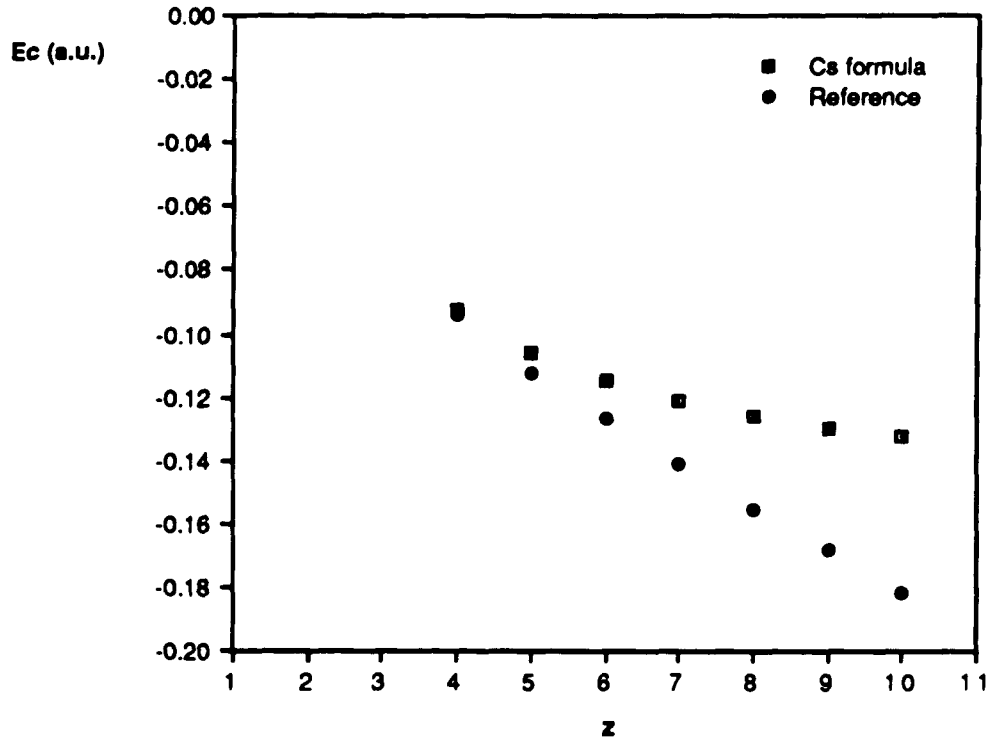


Table 5. Correlation energy for the series of ions isoelectronic with beryllium.

	Z	Ec (a.u.) CS formula	Ec (a.u.) Ref.(68,74)	Error (%)
Be	4	-0.092629	-0.0940	1.5
B^{+}	5	-0.105992	-0.1123	5.6
C^{2+}	6	-0.114941	-0.1268	9.4
N^{3+}	7	-0.121298	-0.1412	14.1
O^{4+}	8	-0.125991	-0.1551	18.8
F^{5+}	9	-0.129555	-0.1684	23.1
Ne^{6+}	10	-0.132316	-0.1814	27.1

As the nuclear charge increases, the calculated energies are less accurate for both series. The loss in accuracy is more severe for the beryllium isoelectronic series, where we see errors as large as 27 per cent for Ne^{6+}. Indeed, most of the values in the beryllium isoelectronic series show errors that surpass the highest figure previously reported. These results indicate that, although the formula is remarkably accurate in many cases, there are situations in which its application entails considerable error, namely calculations with ions of moderate nuclear charge.

4. Remarks Regarding the Colle-Salvetti Formalism

The approach of Colle and Salvetti to the correlation problem, starting out with the known Hartree-Fock determinant to end up with a functional for the correlation energy, involves assumptions and approximations. The formalism itself has an empirical character and depends on fitting procedures to fix several parameters. As a consequence of the approximations, the density matrices derived from the correlated wavefunction are not N-representable.(71)

Regarding this point, Cohen et al.(72) 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 which is non N-representable is still capable of yielding good results, as long as the non N-representable part is a small correction to the N-representable part. Following this argument one may think that this is the case of the two-body density matrix derived by Colle and Salvetti, the Hartree-Fock density matrix being the N-representable part, and the non N-representability introduced by the approximations being a small contribution.

We also note that the fundamental assumption expressed in equation (53) impose limitations on the information one may get from the formalism. Equating the Hartree-Fock one-body density matrix to the exact one-body density matrix is equivalent to neglecting the kinetic energy contribution to Ec, and the correlation correction to any other momentum dependent property.

The Hartree-Fock wavefunction and the exact wavefunction both satisfy the virial theorem. Thus, we would expect the correlation correction to the potential energy and the total correlation energy to be related by the virial theorem as well. But we cannot verify this point since the correlation energy obtained by equation (57) can not be broken down into a potential- and a kinetic-energy contribution.

CHAPTER 3 APPROXIMATELY N-REPRESENTABLE DENSITY MATRICES AND CORRELATION ENERGY

1. Our Goals in the Context of Density Functional Theory

This chapter is concerned with the derivation of first- and second-order density matrices approximately N-representable by a correlated determinant wavefunction whose reference state is the exact density determinant; and with the calculation of the correlation energy using the density matrices derived and a generalized definition of the correlation energy to include any single determinant wavefunction.

The importance of choosing the exact density determinant as the reference state is better understood when placed within the context of density functional theory. Therefore, we briefly review a fundamental theorem in density functional theory.

The Hohenberg and Kohn (HK) theorem(1) states that the electron density contains the information required to determine every property of a system in its ground state. The theorem is proved by 'reductio ad absurdum', and we can outline it as follows.

Suppose, for a non degenerate ground-state, different external potentials, V_1 and V_2, could give rise to the same

density, $\rho(\vec{r})$. Consider two Hamiltonians, H_1 and H_2, with eigenfunctions Ψ_1 and Ψ_2 respectively, that differ only by their external potentials,

$$H_1 - H_2 \equiv V_1 - V_2 \tag{59}$$

Then

$$\langle \Psi_1 | H_1 - H_2 | \Psi_1 \rangle = E_1 - E_2[\Psi_1] \tag{60}$$

and

$$\langle \Psi_2 | H_1 - H_2 | \Psi_2 \rangle = E_1[\Psi_2] - E_2 \tag{61}$$

where E_1 and E_2 are the eigenvalues of H_1 and H_2 respectively, $E_2[\Psi_1]$ is an estimate of the eigenvalue of H_2 based on the state Ψ_1, and $E_1[\Psi_2]$, is an estimate of the eigenvalue of H_1 based on the state Ψ_2.

According to the variational theorem equations (60) and (61) give

$$E_1 - E_2[\Psi_1] \leq E_1 - E_2 \tag{62}$$

and

$$E_1[\Psi_2] - E_2 \geq E_1 - E_2 \qquad (63)$$

The left-hand side of these inequalities both equal the same number, because

$$\langle\Psi_1|H_1-H_2|\Psi_1\rangle = \int\rho(\bar{r})\ (V_1-V_2)\ d\bar{r} = \langle\Psi_2|H_1-H_2|\Psi_2\rangle \qquad (64)$$

This equation shows a contradiction since one number cannot satisfy both inequalities (62) and (63) simultaneously. The original statement must thus be wrong, there cannot be two different external potentials giving rise to the same density. The density fixes the external potential, which in turn fixes the Hamiltonian, its eigenfunction and every electronic operator property.

At the N-body level, it is obvious that the density is a much simpler object than the wavefunction, and the functional relationships between properties and the density become extremely important. Unfortunately, they are not always known. For example, the universal HK functional(1) for the calculation of the total energy

$$F[\rho] = \langle\Psi[\rho]\ |T+U|\ \Psi[\rho]\rangle \qquad (65)$$

where T and U are the kinetic and electron interaction energies respectively, is still an outstanding problem.

As pointed out in Chapter 1, the single determinant of x-ray orbitals is obtained by minimizing a density functional. It delivers the exact density but, in general, it is not an exact wavefunction. As a means of improving the exact density single determinant we consider the wavefunction

$$\Psi(1,\ldots N) = \Psi_{\underline{det}}(1,\ldots N)\prod_{i<j}(1-\varphi(ij)) \qquad (66)$$

where the exact density determinant is multiplied by a spinless two-particle correlation function, symmetric in the coordinates of a particle pair. This type of wavefunction, referred to as correlated determinant wavefunction (CDWF), containing explicit dependence on interparticle distance coordinates, is capable of yielding very accurate results.(45-50,75)

The full N-body wavefunction though, carries more information than is needed to calculate observed properties. Since the usual Hamiltonian contains only one- and two-body terms, reduction from a N-body to a two-body description loses no information.(73)

In the next section the one- and two-body reduced density matrices will be obtained from the wavefunction in equation (66), by following the usual definitions for reduced density matrices. In obtaining the reduced density matrices we will make some approximations, and this brings

about the problem of N-representability. Therefore, conditions will be set to ensure approximate N-representability.

2. Derivation of the One-body and Two-body Reduced Density Matrices

The first and second-order reduced spinless density matrices are derived from the correlated determinant wavefunction(66)

$$\Psi(1,2,\ldots N) = \Psi_{\underline{det}}(1,2,\ldots N) \prod_{i<j} (1- \varphi(ij)),$$

following McWeeny's formalism(17). The square of the wavefunction is integrated over the spatial coordinates of N-1 and N-2 particles, respectively, and the spin coordinates of all the particles.

The square of the wavefunction is

$$\Psi^*(1,\ldots N)\, \Psi(1',\ldots N) = \Psi^*_{\underline{det}}(1,\ldots N)\, \Psi_{\underline{det}}(1',\ldots N) \prod_{i<j} (1+b(iji'j')) \qquad (67)$$

where

$$b(iji'j') \equiv -\varphi(ij) - \varphi(i'j') + \varphi(ij)\,\varphi(i'j') \qquad (68)$$

As a matter of convenience, the product of the correlation functions in equation (67) can be written as

$$\prod_{i<j}(1+b(ij)) = 1 + \sum_{i<j} b(ij) + \sum_{\substack{i<j,k<l \\ (ij)<(kl)}} b(ij)\; b(kl) + \ldots \qquad (69)$$

and the square of the wavefunction, as

$$\Psi^*(1,\ldots N)\,\Psi(1',\ldots N') = \Psi^*_{\underline{det}}(1,\ldots N)\,\Psi_{\underline{det}}(1',\ldots N')$$

$$(1+\Sigma b+\Sigma bb+\ldots) \qquad (70)$$

Neglecting all the terms that contain products of b's in the equation above, we get

$$\Psi^*(1,\ldots N)\,\Psi(1',\ldots N') \cong \Psi^*_{\underline{det}}(1,\ldots N)\,\Psi_{\underline{det}}(1',\ldots N')$$

$$(1+\sum_{i<j} b(ij)) \qquad (71)$$

With this approximate form of the square of the wavefunction, the spinless first-order density matrix is

$$P_1(11') = P_{1\underline{det}}(11') + N\int \Psi^*_{\underline{det}}(1,\ldots N)\, \Psi_{\underline{det}}(1',\ldots N) \sum_{i<j} b(ij)\; d2\ldots N\; ds \qquad (72)$$

and the diagonal element of the spinless second-order density matrix is

$$P_2(1212) = P_{2\underline{det}}(1212) + N\,(N-1)\int \Psi^*_{\underline{det}}(1,\ldots N)\, \Psi_{\underline{det}}(1,\ldots N) \sum_{i<j} b(ij)\; d3\ldots N\; ds \qquad (73)$$

It was discussed in Chapter 1 that the conditions for N-representability of the density and of the first-order density matrix by a single Slater determinant have been established. However, N-representability of the second-order density matrix is not a completely solved problem yet.

We recall that in the usual Hamiltonian only one- and two-body terms are included. Therefore, the second-order density matrix is the fundamental object in the calculation

of the energy. Moreover, it has been shown that the variation principle, which allows for the calculation of an upper bound to the energy for every second-order density matrix, holds as long as N-representability is satisfied.(18,84,85)

For the exact density determinant we have

$$P_1(11'|\vec{1},\vec{1}') = P_{1\underline{det}}(11'|\vec{1},\vec{1}') \qquad (74)$$

and consequently

$$\int \Psi^*_{\underline{det}}(1,\ldots N)\, \Psi_{\underline{det}}(1,\ldots N)\, \sum_{i<j} b(ij)\, d2\ldots N\, ds = 0 \qquad (75)$$

From the last equation we derive conditions for approximate CDWF N-representability of the density matrices (72) and (73).

The product $\Psi^*_{\underline{det}} \cdot \Psi_{\underline{det}}$ can be removed from the integral in equation (75) by Taylor series expanding the interparticle coordinate dependence up to zeroth order, a reasonable approximation if the correlation function decreases rapidly when the distance between the particles increases. We take the alternative form of the summation

$$\sum_{i<j} b(ij) = \sum_{\substack{k>1 \\ l>k}} (b(1k)+b(kl)) \tag{76}$$

and interchange the summation with the integral in equation (75) to obtain

$$\sum_{\substack{k>1 \\ l>k}} (b(1k)+b(kl))\ d2...N = 0 \tag{77}$$

A change of variables in equation (77) according to the definitions

$$\bar{r} = \bar{r}_i - \bar{r}_j \qquad \text{and} \qquad \bar{R} = \frac{1}{2}(\bar{r}_i + \bar{r}_j) \tag{78}$$

yields

$$(N-1) \int b(\bar{R},\bar{r})\ d\bar{r} + \frac{(N-1)\ (N-2)}{2} \int d\bar{R} \int b(\bar{R},\bar{r})\ d\bar{r} = 0 \tag{79}$$

which holds if

$$\int b(\bar{R},\bar{r})\ d\bar{r} = 0 \tag{80}$$

Then, within the approximations mentioned before, equation (80) is sufficient for CDWF N-representability. Now, we enforce condition (80) to obtain $P_1(11')$ and $P_2(1212)$. Equation (73) can be written in the form

$$P_2(1212) = P_{2\underline{det}}(1212)\ (1+b(1212))+N\ (N-1)\int \Psi^*_{\underline{det}}(1,\ldots N)$$

$$\Psi_{\underline{det}}(1,\ldots N)\ \sum_{\substack{k>2\\ l>k}}(b(1k)+b(2k)+b(kl))\ d3\ldots N\ ds \tag{81}$$

By Taylor series expanding to zeroth order the product $\Psi^*_{\underline{det}}\cdot\Psi_{\underline{det}}$ and using equation (80), the second term on the right-hand side of equation (81) vanishes and $P_2(1212)$ becomes

$$P_2(1212) = P_{2\underline{det}}(1212)\ (1+b(1212)) \tag{82}$$

For the one-body density matrix equation (72) can be expressed as

$$P_1(11') = P_{1\underline{det}}(11')+N\int \Psi^*_{\underline{det}}(1,\ldots N)\ \Psi_{\underline{det}}(1',\ldots N)$$

$$\sum_{\substack{k>1\\ l>k}}(b(1k1'k)+b(kl))\ d2\ldots N\ ds \tag{83}$$

which is equivalent to

$$P_1(11') = P_{1\underline{det}}(11') + N\sum_{k>1}\int \Psi^*_{\underline{det}}(1,\ldots N)\,\Psi_{\underline{det}}(1',\ldots N)\,b(1k1'k)\,d2\ldots N\,ds + N\sum_{\substack{k>1\\ l>k}}\int \Psi^*_{\underline{det}}(1,\ldots N)\,\Psi_{\underline{det}}(1',\ldots N)\,b(kl)\,d2\ldots N\,ds \qquad (84)$$

According to equations (77) to (80), the third term on the right-hand side of equation (84) goes to zero after Taylor-series expansion to zeroth order of the product $\Psi^*_{\underline{det}}\cdot\Psi_{\underline{det}}$. And for the second term we have

$$\sum_{k>1}\int \Psi^*_{\underline{det}}(1,\ldots N)\,\Psi_{\underline{det}}(1',\ldots N)\,b(1k1'k)\,d2\ldots N\,ds = (N-1)\int \Psi^*_{\underline{det}}(1,\ldots N)\,\Psi_{\underline{det}}(1',\ldots N)\,b(121'2)\,d2\ldots N\,ds \qquad (85)$$

Then, equation (84) becomes

$$P_1(11') = P_{1\underline{det}}(11') + \int P_{2\underline{det}}(121'2)\,b(121'2)\,d2 \qquad (86)$$

with

$$\int P_{2\underline{det}}(1212)\ b(1212)\ d2 = 0 \qquad (87)$$

for its diagonal element.

The solution of equation (87) provides a way to determine b by adopting a specific form for the correlation function, $\varphi(12)$. We use the same functional form as the one used by Colle and Salvetti(56),

$$\varphi(12) = \exp(-\beta^2 r^2)\ (1-\Phi(\bar{R})\ (1+r/2)) \qquad (88)$$

because it allows the wavefunction to satisfy the cusp condition(64) for any $\bar{r}_i \to \bar{r}_j$, and to become a single Slater determinant when the electrons are far apart. Additionally, the exponential factor makes the correlation function drop off sharply with the increasing of the interparticle distance which is consistent with the short-range nature of Coulomb correlation.

The quantity $\beta(\bar{R})$ is a functional of the density obtained by following the same dimensional argument explained in Chapter 2.

$$\beta(\bar{R}) = q\ \rho^{\frac{1}{3}}(\bar{R}) \qquad (89)$$

The parameter q is to be fixed variationally.

To obtain $\Phi(\bar{R})$ from equation (87) the variable of integration $\bar{r}_2$ is changed to $\bar{r}$, and $P_{2\underline{det}}$ is expanded in a Taylor series about $\bar{r}=0$ up to zeroth order. Then,

$$\int (\varphi^2(12) - 2\,\varphi(12))\, d\bar{r} = 0 \tag{90}$$

which we further approximate by

$$\int \varphi(12)\, d\bar{r} = 0 \tag{91}$$

From the latter equation follows

$$(1-\Phi(\bar{R})) \int \exp(-\beta^2 r^2)\, d\bar{r} - \frac{\Phi(\bar{R})}{2} \int r \exp(-\beta^2 r^2)\, d\bar{r} = 0 \tag{92}$$

Using the integrals of Appendix C in equation (92), we get

$$\frac{\pi^{3/2}}{\beta^3} = \Phi(\bar{R}) \frac{\pi^{3/2}}{\beta^3} + \Phi(\bar{R}) \frac{\pi}{\beta^4} \tag{93}$$

and solving for $\Phi(\bar{R})$ we obtain

$$\Phi(\bar{R}) = \frac{\sqrt{\Pi}\,\beta(\bar{R})}{1+\sqrt{\Pi}\,\beta(\bar{R})} \qquad (94)$$

The existence of and the method to obtain the "exact density" orbitals and the related density matrices, $P_{1\underline{det}}$ and $P_{2\underline{det}}$, have been discussed in Chapter 1.

Equations (82) and (86) for $P_2(1212)$ and $P_1(11')$ are important since they are the objects that are necessary to evaluate all the electronic properties of a system.

3. Calculation of the Correlation Energy: Beryllium Atom - A Test Calculation

The approximately N-representable density matrices derived in section 2 will be used in this section to calculate correlation energies. As a test calculation, the correlation energy of the beryllium atom is evaluated.

The definition of the correlation energy in its generalized form is

$$Ec = E_{exact} - E_{det} \qquad (95)$$

where E_{exact} is the eigenvalue of the non-relativistic Hamiltonian and E_{det} is the energy computed with any single determinant wavefunction.

We consider the particular definition

$$Ec = E_{exact} - E_{\underline{det}} \tag{96}$$

where $E_{\underline{det}}$ is the energy calculated with a single determinant of x-ray orbitals or "exact density" determinant.

The usual form of the Hamiltonian, H, containing only one- and two-body terms, h_i and h_{ij}, is

$$H = \Sigma_i h_i + \Sigma_{i<j} h_{ij} \tag{97}$$

The expectation value of H is then

$$E = \int h_1 \; P_1(11'\Big|_{1'\to 1} d\bar{r}_1 + \frac{1}{2}\int h_{12} \; P_2(1212) \; d\bar{r}_1 \; d\bar{r}_2 \tag{98}$$

and $E_{\underline{det}}$ is given by

$$E_{\underline{det}} = \int h_1 \; P_{1\underline{det}}(11'\Big|_{1'\to 1} d\bar{r}_1 + \frac{1}{2}\int h_{12} \; P_{2\underline{det}}(1212) \; d\bar{r}_1 \; d\bar{r}_2 \tag{99}$$

In atomic units the operators h_1 and h_{12} are

$$h_1 = -\tfrac{1}{2}\nabla_1^2 - Z/r_1$$

$$h_{12} = \frac{1}{|\bar{r}_1 - \bar{r}_2|} \qquad (100)$$

Substitution in equation (98) of $P_2(1212)$ and $P_1(11')$ by expressions (82) and (86) respectively, and the use of equation (96) result in the formula

$$Ec = -\tfrac{1}{2}\int \nabla_1^2 (P_{2\underline{det}}(121'2)\ b(121'2))\Big|_{1'\to 1} d\bar{r}_1\ d\bar{r}_2 + \tfrac{1}{2}\int P_{2\underline{det}}(1212)\ b(1212)\ \frac{1}{|\bar{r}_1 - \bar{r}_2|}\ d\bar{r}_1\ d\bar{r}_2 \qquad (101)$$

The first term on the right-hand side of the equation above represents the kinetic-energy contribution and the second term, the potential-energy contribution arising from interelectronic repulsion. We therefore define

$$Tc \equiv -\frac{1}{2}\int \nabla_1^2 (P_{2\underline{det}}(121'2)\ b(121'2))\Big|_{1'\to 1} d\bar{r}_1\ d\bar{r}_2 \qquad (102)$$

and

$$Vc = \frac{1}{2} \int P_{2\underline{det}}(1212)\ b(1212)\ \frac{1}{|\bar{r}_1 - \bar{r}_2|}\, d\bar{r}_1\ d\bar{r}_2 \qquad (103)$$

so that

$$Ec = Tc + Vc \qquad (104)$$

We note that the form of the correlation energy given by equation (101) is a functional of the density, because $P_{2\underline{det}}$ and b are both functionals of the density.

As an example of the use of equation (101) the correlation energy of beryllium in its ground state is calculated. For the sake of simplicity a closed-shell system has been chosen. Moreover, the x-ray orbitals of beryllium are readily available.(67) The P-matrix is shown in table 6 and the Clementi(69) basis set of six normalized Slater type orbitals (two 1s and four 2s) is listed in table 7.

Table 6. Be atom P-matrix. Ref.(67)

.8537230					
.0857245	.0086220				
-.0038610	-.0006750	.0137480			
-.1297760	-.0107280	-.1092420	0.8953890		
-.0757950	-.0070445	-.0267050	0.2267550	.0595630	
.0382130	.0036950	.0068270	-.0614970	-.0170600	.0052480

Table 7. Be atom Clementi's basis functions. Ref.(69)

$$\psi_i = \frac{(2\zeta_i)^{n_i+1/2}}{2(\pi(2n_i)!)^{1/2}} r^{n_i-1} \exp(-\zeta_i r)$$

i	n_i	ζ_i
1	1	3.470300
2	1	6.368100
3	2	0.7516000
4	2	0.9084000
5	2	1.423600
6	2	2.761600

In this section the procedure to obtain Ec is outlined. Equation (101) is implemented in a zeroth-order approximation, that is, the Taylor series expansions of $P_{2\underline{det}}$ and its derivatives are truncated at the zeroth-order term. The details of all the calculations performed are described in Appendix C.

We start by changing the variables of integration $\bar{r}_1$ and $\bar{r}_2$ to $\bar{r}$ and $\bar{R}$ using the definitions in equation (78) to get

$$Tc = -\frac{1}{2}\int (\nabla_1^2 P_{2\underline{det}}(121'2)_{1,\underrightarrow{|}1} b(1212) + 2\,\nabla_1 P_{2\underline{det}}(121'2)_{1,\underrightarrow{|}1} \cdot \nabla_1 b(121'2)_{1,\underrightarrow{|}1} + P_{2\underline{det}}(1212)\,\nabla_1^2 b(121'2)_{1,\underrightarrow{|}1})\, d\bar{r}\, d\bar{R} \tag{105}$$

and

$$Vc = \frac{1}{2}\int P_{2\underline{det}}(1212)\; b(1212)\; \frac{d\bar{r}}{r}\, d\bar{R} \tag{106}$$

Then, we expand $P_{2\underline{det}}$ and its derivatives in a Taylor series about $\bar{r}=0$ and retain only the leading terms. In this way, $P_{2\underline{det}}$ and its derivatives become functions of $\bar{R}$ only.

Recalling equations (68) and (88) it is easy to see that all the integrals over $\bar{r}$ can be evaluated analytically. A numerical integration over $\bar{R}$ is carried out by the trapezoidal rule.

In the previous section it was stated that the parameter q was to be determined variationally. Accordingly, Ec was calculated for different values of q to find the minimum. The results of these calculations are

presented in table 8 and a plot of Ec versus q is shown in figure 5.

Figure 5. Be atom (exact density). Total correlation energy, kinetic and potential energy contributions as functions of q.

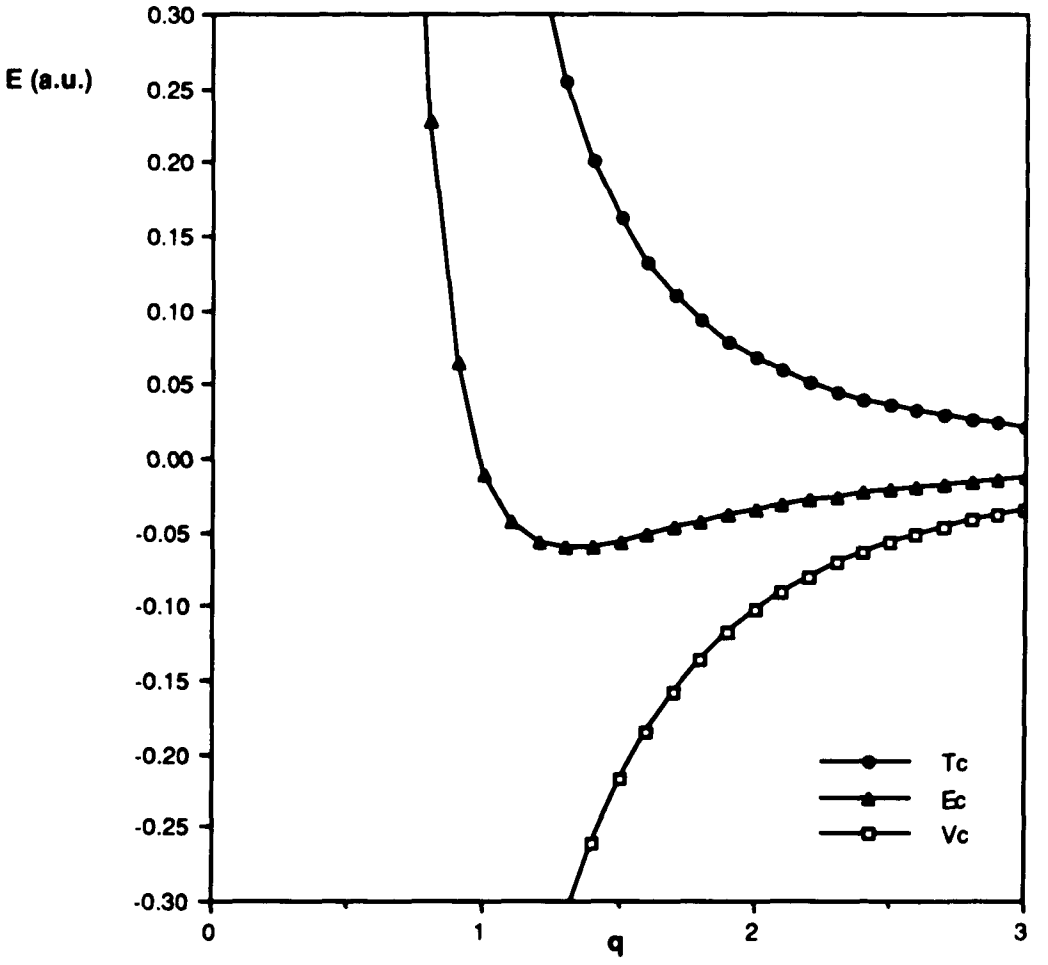


Table 8. Be atom (exact density). Total correlation energy, kinetic and potential energy contributions as functions of q. Ec, Tc and Vc are in atomic units.

q	Tc	Vc	Ec
0.50	7.047223	-3.360864	3.686359
0.60	3.625387	-2.167452	1.457934
0.70	2.082910	-1.488520	0.594390
0.80	1.299045	-1.071126	0.227919
0.90	0.862943	-0.799121	0.063823
1.00	0.602508	-0.613611	-0.011103
1.10	0.437876	-0.482383	-0.044507
1.20	0.328841	-0.386723	-0.057882
1.30	0.253771	-0.315216	-0.061445
1.40	0.200367	-0.260608	-0.060241
1.50	0.161301	-0.218133	-0.056832
1.60	0.132028	-0.184561	-0.052533
1.70	0.109631	-0.157652	-0.048021
1.80	0.092180	-0.135814	-0.043633
1.90	0.078363	-0.117892	-0.039529
2.00	0.067265	-0.103038	-0.035773
2.10	0.058239	-0.090616	-0.032377
2.20	0.050813	-0.080142	-0.029329
2.30	0.044642	-0.071245	-0.026603
2.40	0.039466	-0.063637	-0.024171
2.50	0.035087	-0.057089	-0.022002
2.60	0.031356	-0.051421	-0.020066
2.70	0.028153	-0.046490	-0.018337
2.80	0.025387	-0.042177	-0.016790
2.90	0.022984	-0.038389	-0.015405
3.00	0.020885	-0.035047	-0.014162

The Ec-curve has a minimum at q=1.31 for which Ec= -0.0614825 a.u. The formula is capable of computing 65 per cent of the correlation energy. This is an excellent result if one considers that the simplest possible approximation has been used in the evaluation of the integrals of equations (105) and (106).

Addition of this value of the correlation energy to the energy calculated with the exact density single determinant (see table 1) gives a total energy E= -14.63298 a.u. As a matter of comparison, a set of total energy data for beryllium, calculated by CI and other methods, is shown in table 9.

Table 9. Some results of 'ab initio' calculations of the energy of the beryllium atom in its ground state.

CI-calculations		
	Watson (79)	-14.65740 a.u.
	Weiss (80)	-14.66090 a.u.
Perturbation Theory		
	Kelly (81)	-14.66398 a.u.
	Nesbet (82)	-14.66515 a.u.
Hilleraas-type functions		
	Szasz and Byrne (83)	-14.65740 a.u.

The whole calculation of the correlation energy, based on the formulas (105) and (107), requires very little computer time as opposed to other methods currently in use.

The value of Vc is added to $V_{\underline{det}}$ and the value of Tc is added to $T_{\underline{det}}$ (see table 1) to study the behavior of the obtained results in relation to the virial theorem

$$\frac{Tc + T\underline{det}}{Vc + V\underline{det}} = -\frac{14.8467}{29.4796} = -0.5036$$

Although this is not the exact value of -0.5 corresponding to the ratio of the exact T and V, it is very close to it. In fact, we do not have reasons to expect the exact ratio since, with this level of approximation, not one hundred per cent of the correlation energy has been computed.

4. Test of the Correlation Energy Formalism Based on Hartree-Fock Density

The present formalism is based on the approximate N-representability condition imposed on the first- and second-order density matrices by the fact that the single-determinant of x-ray orbitals delivers the exact density. Considerable numerical experience indicates that the Hartree-Fock density is very accurate. Therefore, it is reasonable to assume that it can be utilized in the formula for Ec. To test this idea, the correlation energy for beryllium was calculated using the Hartree-Fock density, on the same set of basis functions as the one in section 3 above.

The results are indeed very similar to those obtained with the exact density determinant. They are listed in table 10 and plotted in figure 6. The value of the correlation energy is slightly better when calculated with x-ray orbitals. This is in accord with the concept that the

present formula for Ec is a functional of the density. Consequently, similar densities should yield results of comparable accuracy.

Figure 6. Be atom (HF-density). Total correlation energy, kinetic and potential energy contributions as functions of q.

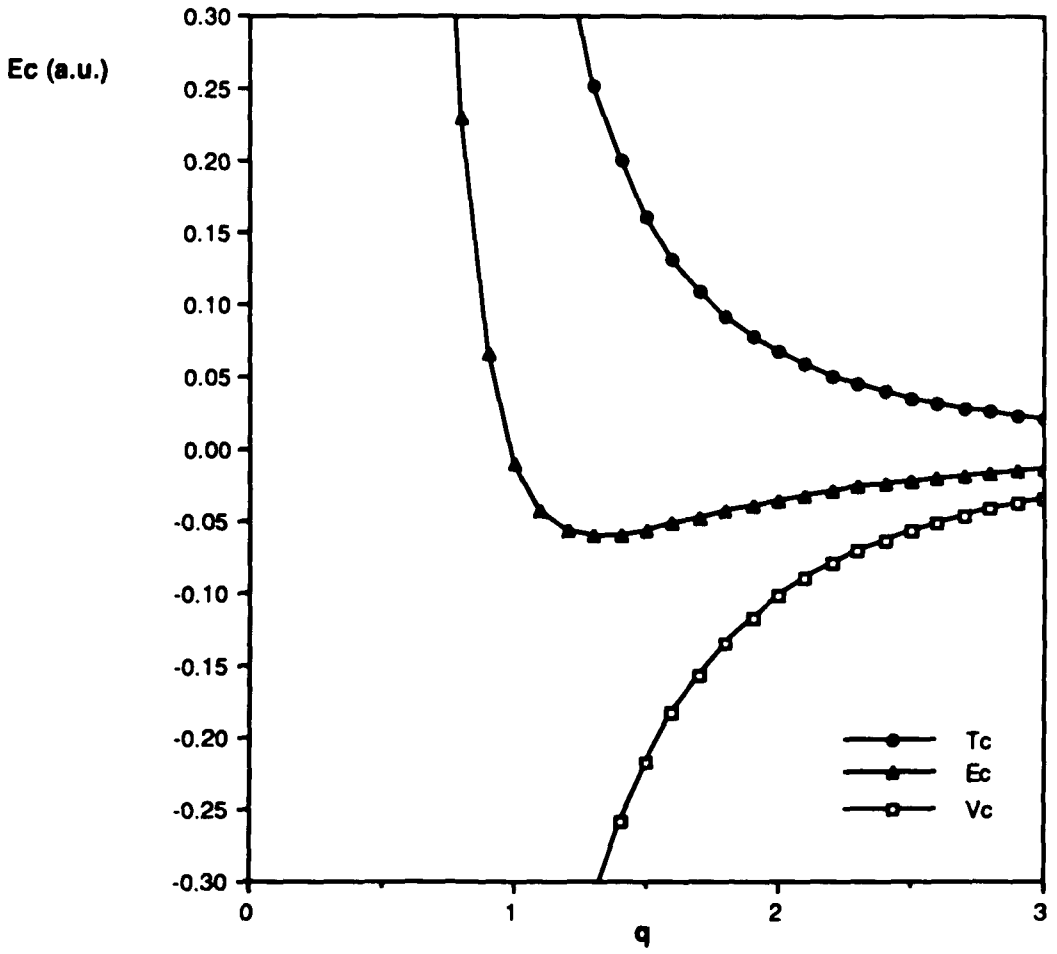


Table 10. Be atom (HF-density). Total correlation energy, kinetic and potential energy contributions as functions of q. Ec, Tc and Vc are in atomic units.

q	Tc	Vc	Ec
0.50	7.029900	-3.344267	3.685633
0.60	3.614849	-2.156345	1.458504
0.70	2.075976	-1.480663	0.595313
0.80	1.294209	-1.065337	0.228872
0.90	0.859416	-0.794718	0.064697
1.00	0.599844	-0.610179	-0.010335
1.10	0.435806	-0.479652	-0.043846
1.20	0.327196	-0.384513	-0.057317
1.30	0.252439	-0.313400	-0.060962
1.40	0.199270	-0.259098	-0.059828
1.50	0.160386	-0.216864	-0.056478
1.60	0.131256	-0.183485	-0.052229
1.70	0.108973	-0.156731	-0.047758
1.80	0.091614	-0.135019	-0.043405
1.90	0.077872	-0.117203	-0.039331
2.00	0.066836	-0.102436	-0.035600
2.10	0.057862	-0.090087	-0.032225
2.20	0.050480	-0.079675	-0.029195
2.30	0.044346	-0.070832	-0.026485
2.40	0.039202	-0.063268	-0.024066
2.50	0.034851	-0.056759	-0.021908
2.60	0.031143	-0.051126	-0.019983
2.70	0.027961	-0.046224	-0.018262
2.80	0.025213	-0.041937	-0.016724
2.90	0.022826	-0.038171	-0.015345
3.00	0.020741	-0.034848	-0.014108

The correlation energy for the helium atom has also been calculated with the Hartree-Fock density(69). The values obtained for Ec, for different values of q, are presented in table 11 and figure 7. The curve has its

minimum at q=1.17, where the correlation energy is

Ec= -0.041882 a.u., and almost reaches the exact value(68).

Figure 7. He atom. Total correlation energy, kinetic and potential energy contributions as functions of q.

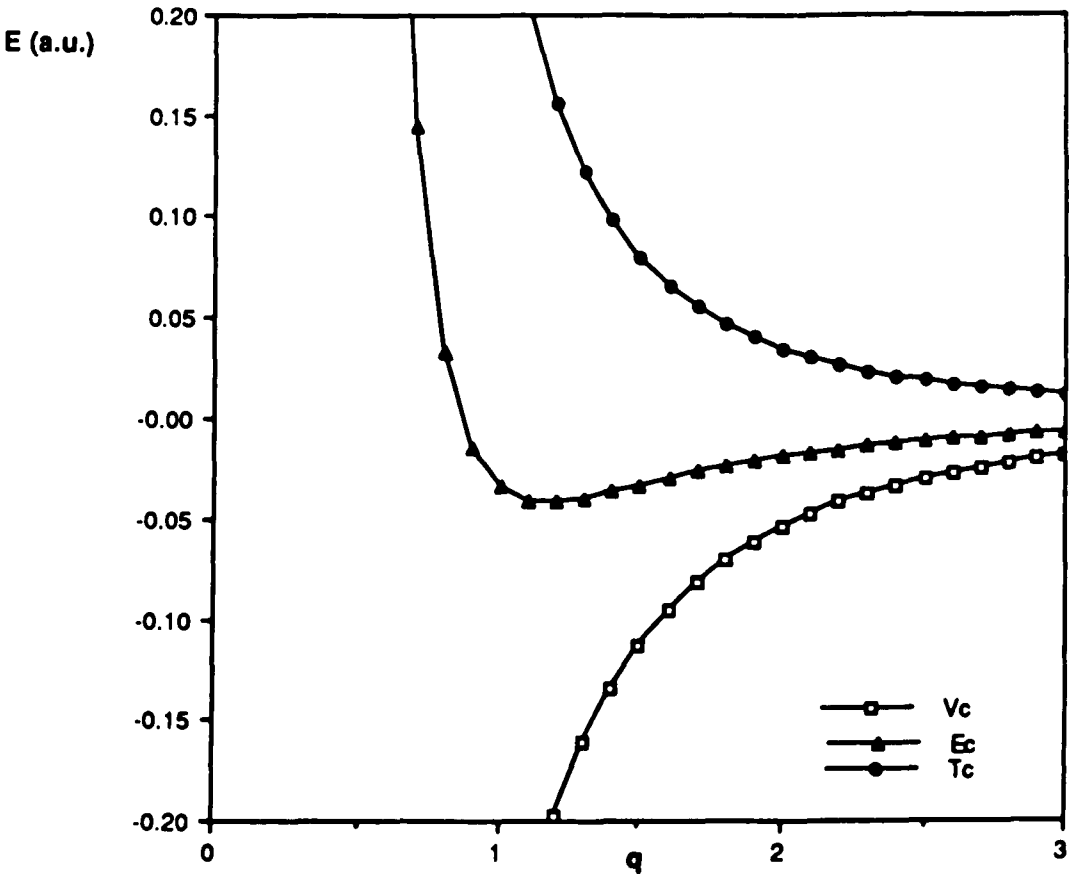


Table 11. He atom. Total correlation energy, kinetic and potential energy contributions as functions of q. Ec, Tc and Vc are in atomic units

q	Tc	Vc	Ec
0.50	2.692057	-1.577929	1.114128
0.60	1.453652	-1.037764	0.415888
0.70	0.869214	-0.724132	0.145082
0.80	0.560554	-0.527934	0.032620
0.90	0.383083	-0.398158	-0.015075
1.00	0.274029	-0.308507	-0.034478
1.10	0.203343	-0.244380	-0.041037
1.20	0.155481	-0.197182	-0.041700
1.30	0.121874	-0.161602	-0.039728
1.40	0.097542	-0.134230	-0.036688
1.50	0.079460	-0.112801	-0.033341
1.60	0.065717	-0.095768	-0.030050
1.70	0.055068	-0.082045	-0.026977
1.80	0.046674	-0.070859	-0.024185
1.90	0.039958	-0.061643	-0.021685
2.00	0.034513	-0.053978	-0.019464
2.10	0.030046	-0.047547	-0.017500
2.20	0.026343	-0.042110	-0.015766
2.30	0.023244	-0.037480	-0.014236
2.40	0.020627	-0.033511	-0.012884
2.50	0.018401	-0.030089	-0.011689
2.60	0.016493	-0.027122	-0.010629
2.70	0.014848	-0.024536	-0.009688
2.80	0.013421	-0.022272	-0.008851
2.90	0.012176	-0.020280	-0.008104
3.00	0.011085	-0.018521	-0.007436

The series of ions isoelectronic with helium and with beryllium were also investigated using the Hartree-Fock density(69) for each ion. The values of Ec at the minimum of the Ec-curve for each ion are shown in Tables 12 and 13, and in figures 8 and 9.

Figure 8. Correlation energy for the series of ions isoelectronic with helium.

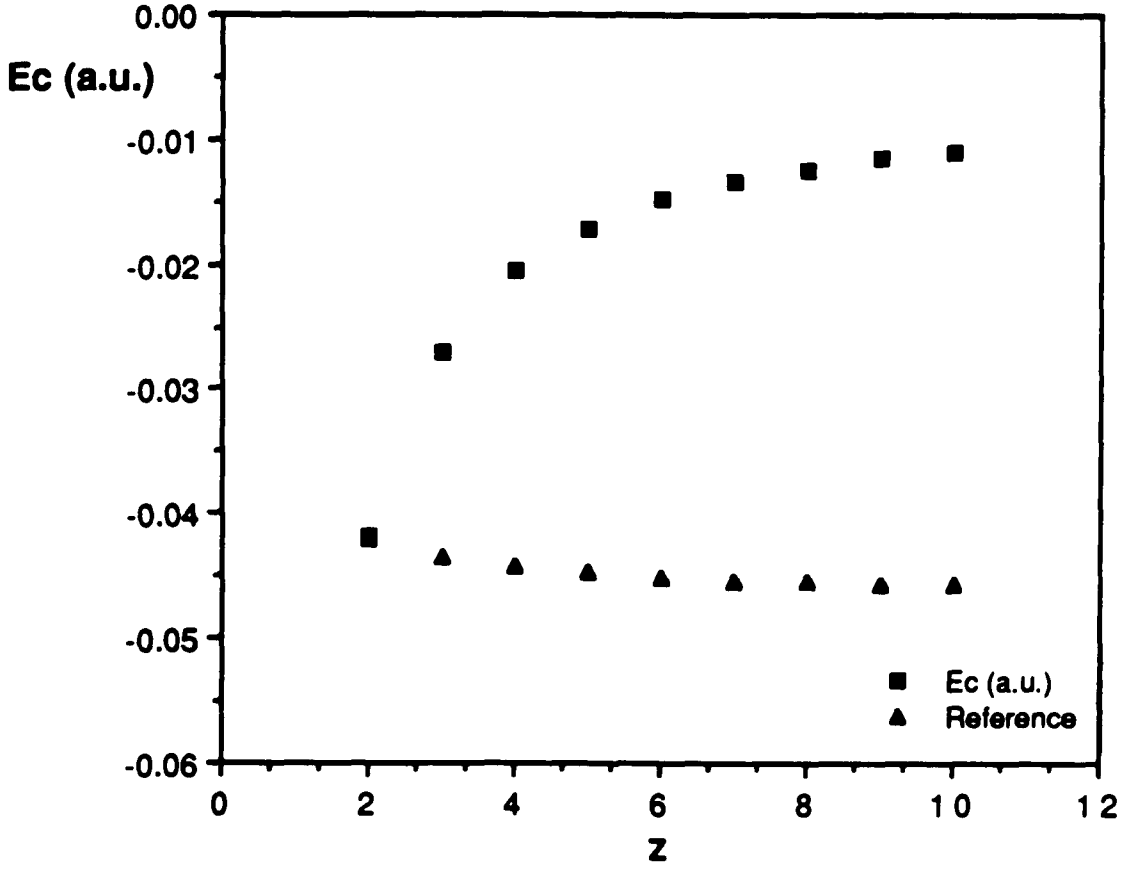


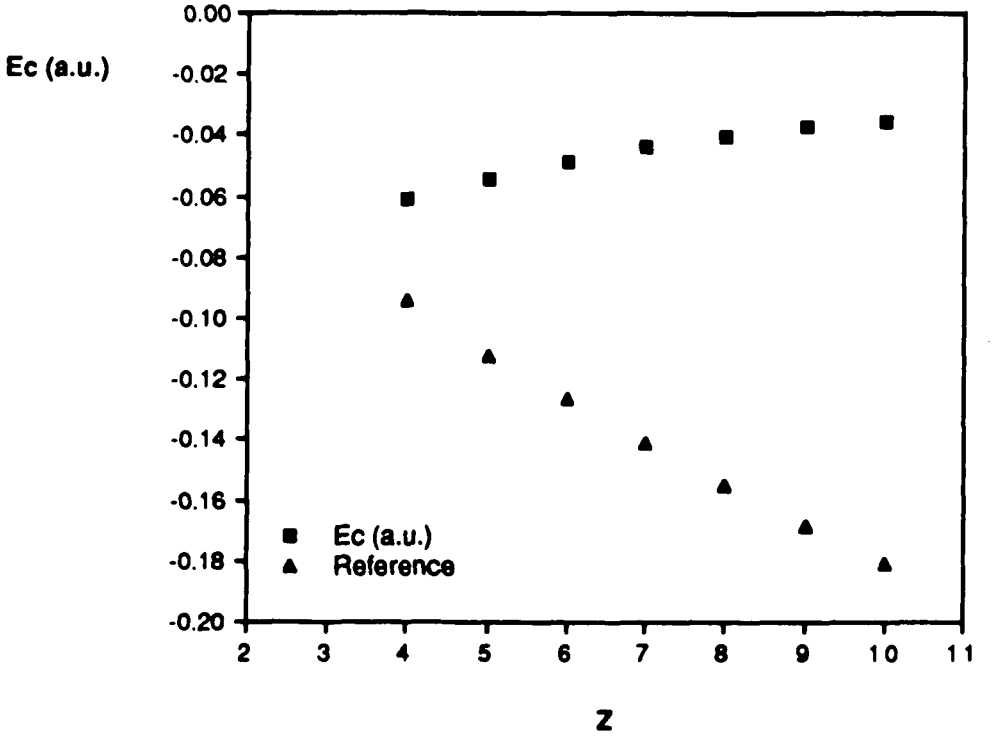
Table 12. Correlation energy for the series of ions isoelectronic with helium.

	Ec (a.u.) This formalism	Ec (a.u.) Ref.[68,74]	% of Ec computed
He	-0.0419	-0.0420	99.8
Li^{+}	-0.0270	-0.0435	62.1
Be^{2+}	-0.0206	-0.0443	46.5
B^{3+}	-0.0171	-0.0448	38.2
C^{4+}	-0.0149	-0.0451	33.0
N^{5+}	-0.0134	-0.0453	29.6
O^{6+}	-0.0124	-0.0455	27.3
F^{7+}	-0.0115	-0.0456	25.2
Ne^{8+}	-0.0109	-0.0457	23.9

Table 13. Correlation energy for the series of ions isoelectronic with beryllium

	Ec (a.u.) This formalism	Ec (a.u.) Ref.[68,74]	% of Ec computed
Be	-0.0615	-0.0944	65.1
B^{+}	-0.0547	-0.1123	48.7
C^{2+}	-0.0489	-0.1268	38.5
N^{3+}	-0.0442	-0.1412	31.3
O^{4+}	-0.0405	-0.1551	26.1
F^{5+}	-0.0376	-0.1684	22.3
Ne^{6+}	-0.0352	-0.1814	19.4

Figure 9. Correlation energy for the series of ions isoelectronic with beryllium



We observe that the results are less accurate as the nuclear charge, Z, increases. This may be due to the fact that a zeroth-order Taylor expansion approximation becomes less accurate as the densities fall off more rapidly with distance. Figures 10 to 12 show the density as a function of the distance to the nucleus, R, for each of the ions in the series.

Figure 10. Helium-like ions: HF-density.

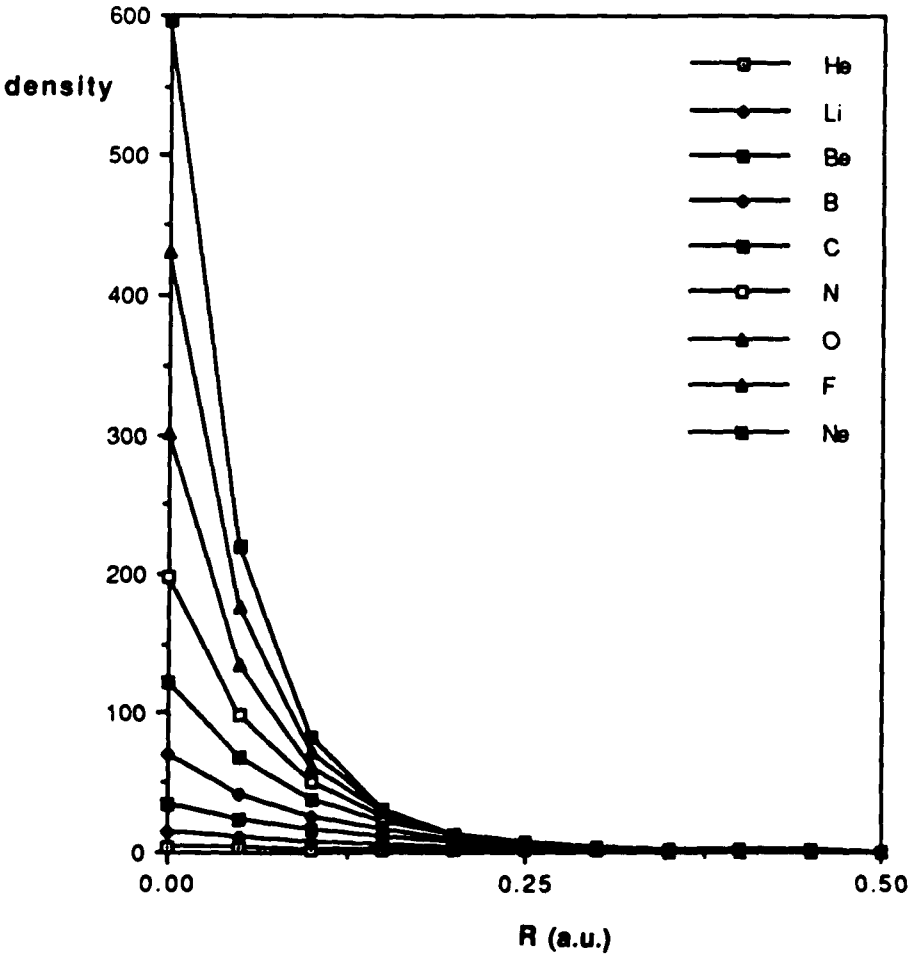


Figure 11. Helium-like ions: HF-density.

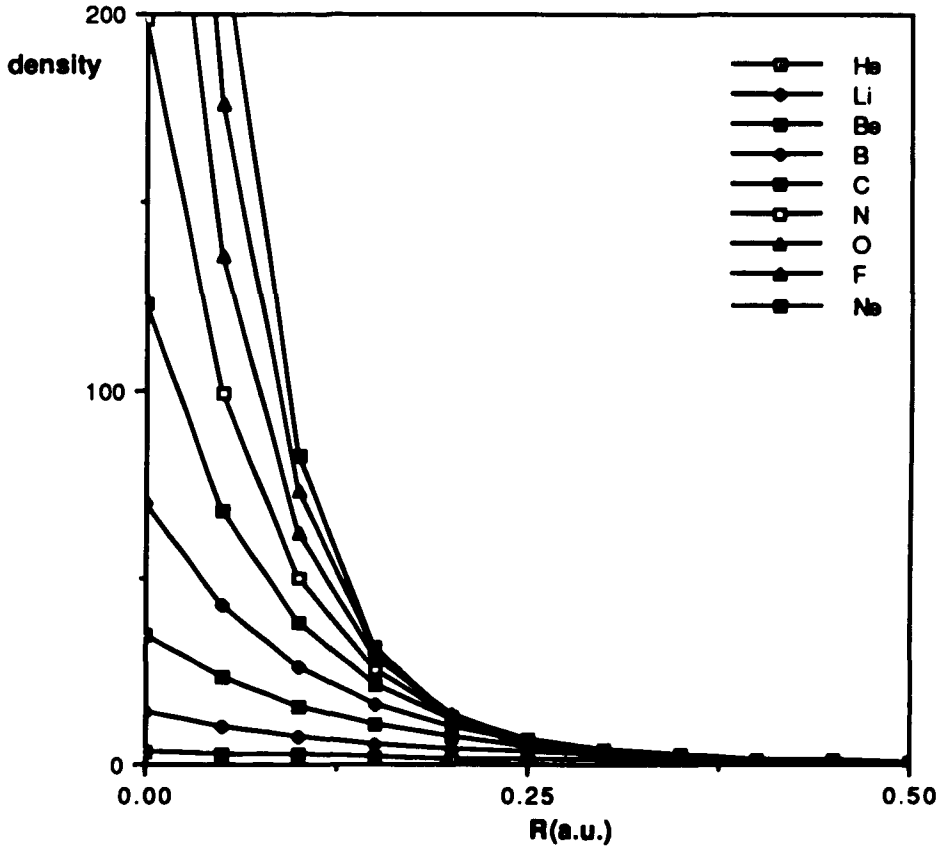
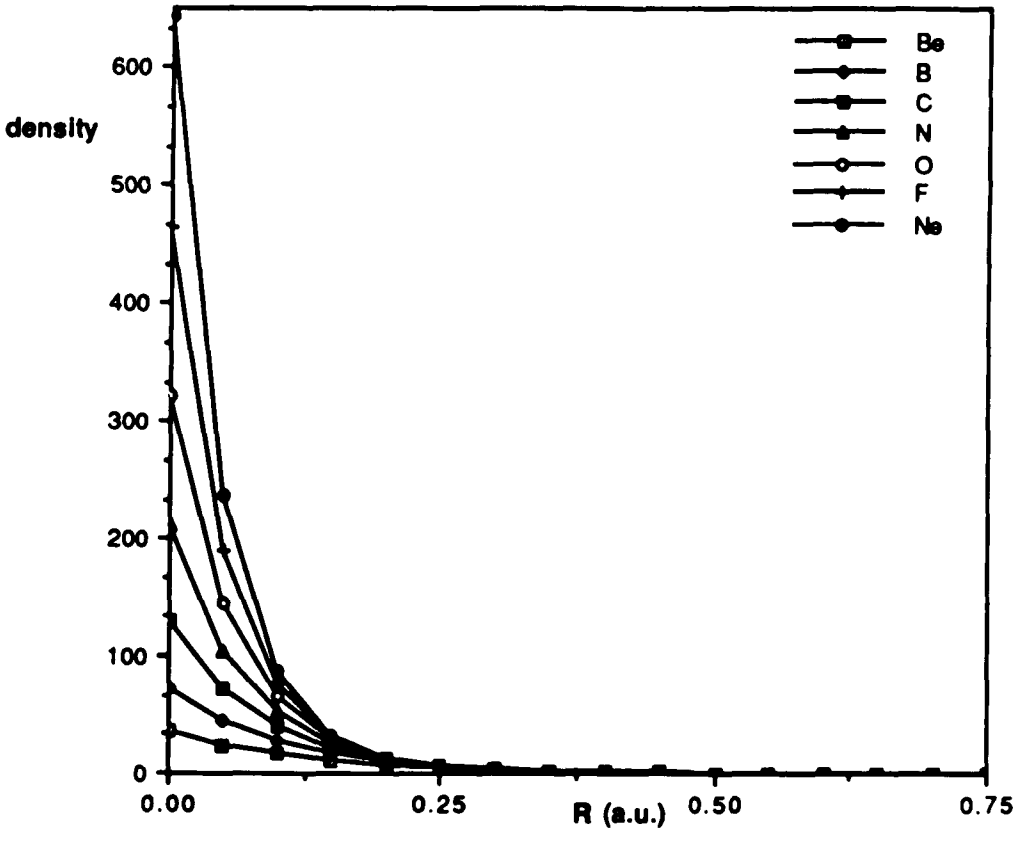


Figure 12. Beryllium-like ions: HF-density.



4. CONCLUSIONS

The problem of correlated x-ray density matrices has been studied within the framework of the correlated-determinant-wavefunction. Numerical evidence and theoretical considerations indicate that this type of wavefunction is capable of yielding very accurate energies.

The Colle-Salvetti formula for the calculation of the correlation energy has been applied to the series of ions isoelectronic with helium and with beryllium. The accuracy of the results decreases with the increasing of the nuclear charge, Z, in both series. The series of beryllium-like ions displays the higher errors. In fact, they can be more than three times higher than previously reported errors. Under stringent conditions, namely highly positive ions, the empirical formula of Colle and Salvetti seems to break down. Nevertheless, it gives excellent estimates of the correlation energy for a number of atoms and small molecules.

The formula of Colle and Salvetti is non-variational(71) and depends on fitting to the helium atom to fix several parameters. However, the quality of some of the results obtained as well as the study of the functional by Cohen and Lee(71) suggest that an efficient modeling of the correlation function has been achieved, at least for the cases in which highly positive ions are not involved.

It is worth noting that this treatment of the correlation effects is limited to the calculation of the correlation energy, and that this quantity is calculated as a whole. Therefore, correlation corrections to the kinetic energy and to momentum dependent properties are not obtainable from the Colle-Salvetti formalism.

The study of the correlation problem with correlated-determinant-wavefunctions whose reference state is an exact density determinant has been undertaken in Chapter 3.

The first- and second-order reduced density matrices are the only information needed when working with the usual Hamiltonian which contains at most two-body interactions. These reduced density matrices were derived by integration of the wavefunction. The approximations used involved neglecting terms nonlinear in the correlation correction factor, b, and the Taylor-series expansion of the square of the wavefunction retaining only the leading term.

The problem of N-representability of the reduced density matrices obtained was also discussed and, within the approximations mentioned before, conditions were set to ensure approximate N-representability. An important consequence of having the exact density determinant as the reference state for the full wavefunction is that it imposes an exact condition on the diagonal element of the second-order density matrix from which the N-representability conditions can be derived with no further assumptions.

The approximately N-representable density matrices depend on two distinct quantities, the exact density determinant and the correlation function. The results of previous work on the exact density determinant, discussed in Chapter 1, show that physically meaningful orbitals which deliver the exact density can be obtained by means of Clinton's equations.

The form of the correlation function can be chosen to be of the same general form as that of Colle and Salvetti, since this functional form allows the wavefunction to display the appropriate limiting behavior. It satisfies the cusp conditions as $\bar{r}_1$ goes to $\bar{r}_2$, and it approaches the single determinant as the interparticle distance increases. Additionally, the exact condition

$$\int P_{2\underline{det}}(1212)\ (\varphi^2(12)-2\ \varphi(12))\ d2 = 0$$

provides a way to completely determine $\varphi(12)$. The only one parameter, q, in the resultant functional form can be fixed variationally.

A formula to calculate the correlation energy based on the approximate N-representable density matrices was implemented at the zeroth order level for the beryllium atom. With this simple approximation, 65 per cent of the correlation energy is computed in about seventy seconds in a MicroVax-II. A very encouraging result when confronted

with the extensive calculations required by other methods to achieve comparable accuracy.

The method described is apparently variational because of the approximate N-representability of the reduced density matrices derived.

Perhaps the most relevant aspect of this formalism is that it provides the correlation correction to the kinetic energy and to any momentum dependent property in addition to the electron-electron repulsion contribution, while some other methods do not, for example the Colle-Salvetti formalism.

The formula derived for the correlation energy is a functional of the density because both the exact density determinant and the correlation function are functionals of the density. On these grounds, the Hartree-Fock determinant which is known to give a very accurate density was also used to calculate the correlation energy of beryllium. As expected, the result was very close to that obtained with the exact density determinant. Extension of this idea to the helium atom allows for the computation of almost 100 per cent of the correlation energy. A result that might be attributed to a better modeling of the correlation function for this particular case, and/or to a better approximation of the correlation energy formula by a zeroth order Taylor-series expansion.

Calculations performed with the series of helium-like ions and of beryllium-like ions are of poorer accuracy,

especially for high values of Z. By observing the sharper decay of the density as the charge of the ion increases, one may conjecture that Taylor-series expansion truncated at the zeroth order term is a less justified approximation for larger values of Z.

These test calculations, performed with the simplest possible approximation, indicate the validity of the underlying ideas of the formalism and motivate further studies.

There are two distinct levels at which approximations enter the formula for the correlation energy, at the level of the wavefunction (or density matrices), and at the level of the actual evaluation of the correlation energy. Both could be improved. A way to improve the latter would be to work with a second-order formula. This is laborious, but possible. At the level of the wavefunction, work can still be done to improve the model of the correlation function.

The extension of the calculations to other systems is also possible. Particularly important is the study of the electron gas, for which the single determinant of orbitals is well known.

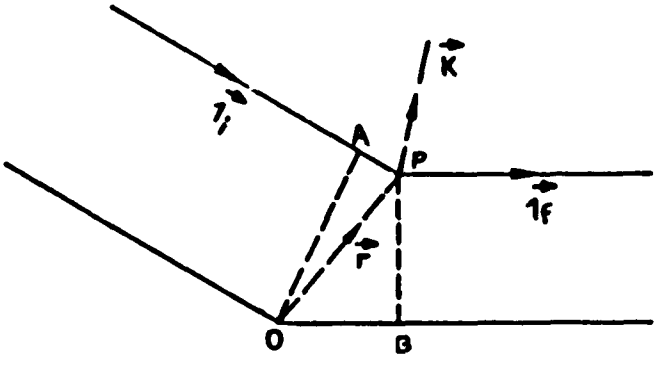
As was pointed out earlier, the information that can be obtained from the present formalism is not restricted to the calculation of the correlation energy. Both the first- and second-order density matrices include correlation effects, and properties in momentum space are therefore also calculable.

A final point to be emphasized is that our formula for the correlation energy, as well as the density matrices involved, are functionals of the density. Hence they enter the domain of density functional theory. As suggested earlier(76,77), the N-representable density matrices could be used to evaluate the universal HK functional, and the correlation potential in the Kohn-Sham equations(78) could be evaluated as a functional derivative of the expression for the correlation energy.

APPENDIX A

Structure Factor, Fourier Transform of the Electron Density

Sketch of the scattering of x-rays by an electron distribution:



The picture above represents two points, O and P, in an electronic charge distribution, separated by the vector $\vec{r}$. The path difference between the radiation scattered by an element of charge at P and the radiation that would be scattered by the same amount of charge located at O, is

$$\overline{OB} - \overline{PA} = \vec{r}\cdot\hat{1}_f - \vec{r}\cdot\hat{1}_i \qquad (A.1)$$

where $\hat{1}_f$ and $\hat{1}_i$ are unit vectors in the directions of the scattered radiation and the incident radiation, respectively. And the phase difference is given by

$$\Phi = \frac{2\pi}{\lambda} \bar{r} \cdot (\hat{1}_f - \hat{1}_i) \qquad (A.2)$$

which can be expressed as

$$\Phi = \bar{K} \cdot \bar{r} \qquad (A.3)$$

with

$$\bar{K} = \frac{2\pi}{\lambda} (\hat{1}_f - \hat{1}_i) \qquad (A.4)$$

The amplitude scattered by the electron distribution respect to the amplitude which would be scattered by an electron at O is, by superposition,

$$F(\bar{K}) = \int \rho(\bar{r}) \exp(i \bar{K} \cdot \bar{r}) \, d\bar{r} \qquad (A.5)$$

where $\rho(\bar{r})\, d\bar{r}$ is the probability of finding the electron in the volume element dr.

APPENDIX B

Derivation of the W factor in the Colle-Salvetti Formula

$$\bar{r} = \bar{r}_1 - \bar{r}_2 \qquad \text{and} \qquad \bar{R} = \frac{1}{2}(\bar{r}_1 + \bar{r}_2) \tag{B.1}$$

$$\bar{r}_1 = \bar{R} + \bar{r}/2 \qquad \text{and} \qquad \bar{r}_2 = \bar{R} - \bar{r}/2 \tag{B.2}$$

$$\begin{aligned} r_1 &\equiv (x_1^2 + y_1^2 + z_1^2) \\ r_2 &\equiv (x_2^2 + y_2^2 + z_2^2) \\ r &\equiv (x^2 + y^2 + z^2) \\ R &\equiv (X^2 + Y^2 + Z^2) \end{aligned} \tag{B.3}$$

where

$$\begin{aligned} x &= x_1 - x_2 & X &= (x_1 + x_2)/2 \\ y &= y_1 - y_2 & Y &= (y_1 + y_2)/2 \\ z &= z_1 - z_2 & Z &= (z_1 + z_2)/2 \end{aligned} \tag{B.4}$$

and conversely

$$x_1 = X+x/2 \qquad x_2 = X-x/2$$

$$y_1 = Y+y/2 \qquad y_2 = Y-y/2 \qquad \text{(B.5)}$$

$$z_1 = Z+z/2 \qquad z_2 = Z-z/2$$

$$\nabla_F = \frac{\partial}{\partial x}\hat{i} + \frac{\partial}{\partial y}\hat{j} + \frac{\partial}{\partial z}\hat{k}$$

$$\nabla_F^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad \text{(B.6)}$$

$$\nabla_1 = \frac{\partial}{\partial x_1}\hat{i} + \frac{\partial}{\partial y_1}\hat{j} + \frac{\partial}{\partial z_1}\hat{k}$$

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \qquad \text{(B.7)}$$

$$\nabla_2 = \frac{\partial}{\partial x_2}\hat{i} + \frac{\partial}{\partial y_2}\hat{j} + \frac{\partial}{\partial z_2}\hat{k}$$

$$\nabla_2^2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \qquad \text{(B.8)}$$

$$\nabla_F = \frac{1}{2}(\nabla_1 - \nabla_2)$$

$$\nabla_F^2 = \frac{1}{4}(\nabla_1^2 + \nabla_2^2 - 2\,\nabla_1 \cdot \nabla_2) \qquad \text{(B.9)}$$

From equations (B.3)

$$\frac{\partial r_1}{\partial x_1} = \frac{x_1}{r_1} \qquad \frac{\partial r_2}{\partial x_2} = \frac{x_2}{r_2}$$

$$\frac{\partial r_1}{\partial y_1} = \frac{y_1}{r_1} \qquad \frac{\partial r_2}{\partial y_2} = \frac{y_2}{r_2} \tag{B.10}$$

$$\frac{\partial r_1}{\partial z_1} = \frac{z_1}{r_1} \qquad \frac{\partial r_2}{\partial z_2} = \frac{z_2}{r_2}$$

Evaluation of $(\nabla_{\bar{r}}^2 P_2(1212))_{\bar{r}=0}$:

$$\nabla_{\bar{r}}^2 P_2(1212) = P_1(11)\ \nabla_{\bar{r}}^2 P_1(22) + 2\ \nabla_{\bar{r}} P_1(11) \cdot \nabla_{\bar{r}} P_1(22) +$$

$$P_1(22)\ \nabla_{\bar{r}}^2 P_1(11) - \frac{1}{2}\ P_1(12)\ \nabla_{\bar{r}}^2 P_1(21) -$$

$$\nabla_{\bar{r}} P_1(12) \cdot \nabla_{\bar{r}} P_1(21) - \frac{1}{2}\ P_1(21)\ \nabla_{\bar{r}}^2 P_1(12) \tag{B.11}$$

Using the operator relationships and definitions (B.6) to (B.10)

$$\nabla_{\bar{r}} P_1(11) = \frac{1}{2}\ \nabla_1 P_1(11) \tag{B.12}$$

$$\nabla_{\bar{r}} P_1(22) = -\frac{1}{2}\ \nabla_2 P_1(22) \tag{B.13}$$

$$\nabla_1 P_1(11) = \frac{\partial P_1(11)}{\partial x_1}\,\hat{i} + \frac{\partial P_1(11)}{\partial y_1}\,\hat{j} + \frac{\partial P_1(11)}{\partial z_1}\,\hat{k} \qquad \text{(B.14)}$$

$$\nabla_2 P_1(22) = \frac{\partial P_1(22)}{\partial x_2}\,\hat{i} + \frac{\partial P_1(22)}{\partial y_2}\,\hat{j} + \frac{\partial P_1(22)}{\partial z_2}\,\hat{k} \qquad \text{(B.15)}$$

$$\nabla_{\vec{r}_1} P_1(11) \cdot \nabla_{\vec{r}_2} P_1(22) = -\frac{1}{4}\left(\frac{\partial P_1(11)}{\partial x_1}\,\frac{\partial P_1(22)}{\partial x_2} + \frac{\partial P_1(11)}{\partial y_1}\,\frac{\partial P_1(22)}{\partial y_2} + \frac{\partial P_1(11)}{\partial z_1}\,\frac{\partial P_1(22)}{\partial z_2}\right) \qquad \text{(B.16)}$$

Using the chain rule and the relationships (B.10),

$$\frac{\partial P_1(11)}{\partial x_1} = \frac{\partial P_1(11)}{\partial r_1}\,\frac{x_1}{r_1} \qquad \frac{\partial P_1(22)}{\partial x_2} = \frac{\partial P_1(22)}{\partial r_2}\,\frac{x_2}{r_2}$$

$$\frac{\partial P_1(11)}{\partial y_1} = \frac{\partial P_1(11)}{\partial r_1}\,\frac{y_1}{r_1} \qquad \frac{\partial P_1(22)}{\partial y_2} = \frac{\partial P_1(22)}{\partial r_2}\,\frac{y_2}{r_2} \qquad \text{(B.17)}$$

$$\frac{\partial P_1(11)}{\partial z_1} = \frac{\partial P_1(11)}{\partial r_1}\,\frac{z_1}{r_1} \qquad \frac{\partial P_1(22)}{\partial z_2} = \frac{\partial P_1(22)}{\partial r_2}\,\frac{z_2}{r_2}$$

$$\nabla_{\underline{r}} P_1(11) \cdot \nabla_{\underline{r}} P_1(22) = -\frac{1}{4} \frac{\partial P_1(11)}{\partial r_1} \frac{\partial P_1(22)}{\partial r_2} \frac{(x_1x_2+y_1y_2+z_1z_2)}{r_1 r_2} \quad \text{(B.18)}$$

$$\nabla_{\underline{r}} P_1(11) \cdot \nabla_{\underline{r}} P_1(22) = -\frac{1}{4} \frac{\partial P_1(11)}{\partial r_1} \frac{\partial P_1(22)}{\partial r_2} \cos\theta_{12} \quad \text{(B.19)}$$

$$\nabla_{\underline{r}} P_1(12) = \frac{1}{2} (\nabla_1 P_1(12) - \nabla_2 P_1(12)) \quad \text{(B.20)}$$

$$\nabla_{\underline{r}} P_1(21) = \frac{1}{2} (\nabla_1 P_1(21) - \nabla_2 P_1(21)) \quad \text{(B.21)}$$

$$\nabla_{\underline{r}} P_1(12) \cdot \nabla_{\underline{r}} P_1(21) = \frac{1}{4} (\nabla_1 P_1(12) \cdot \nabla_1 P_1(21) - \nabla_1 P_1(12) \cdot \nabla_2 P_1(21) - \nabla_1 P_1(21) \cdot \nabla_2 P_1(12) + \nabla_2 P_1(12) \cdot \nabla_2 P_1(21)) \quad \text{(B.22)}$$

$$\nabla_1 P_1(12) \cdot \nabla_1 P_1(21) = \frac{\partial P_1(12)}{\partial x_1} \frac{\partial P_1(21)}{\partial x_1} + \frac{\partial P_1(12)}{\partial y_1} \frac{\partial P_1(21)}{\partial y_1} + \frac{\partial P_1(12)}{\partial z_1} \frac{\partial P_1(21)}{\partial z_1} \quad \text{(B.23)}$$

$$\nabla_1 P_1(12) \cdot \nabla_1 P_1(21) = \frac{\partial P_1(12)}{\partial r_1} \frac{\partial P_1(21)}{\partial r_1} \frac{(x_1^2+y_1^2+z_1^2)}{r_1^2} = \frac{\partial P_1(12)}{\partial r_1} \frac{\partial P_1(21)}{\partial r_1} \quad \text{(B.24)}$$

$$\nabla_1 P_1(12) \cdot \nabla_2 P_1(21) = \frac{\partial P_1(12)}{\partial x_1} \frac{\partial P_1(21)}{\partial x_2} + \frac{\partial P_1(12)}{\partial y_1} \frac{\partial P_1(21)}{\partial y_2} + \frac{\partial P_1(12)}{\partial z_1} \frac{\partial P_1(21)}{\partial z_2} \quad \text{(B.25)}$$

$$\nabla_1 P_1(12) \cdot \nabla_2 P_1(21) = \frac{\partial P_1(12)}{\partial r_1} \frac{\partial P_1(21)}{\partial r_2} \frac{(x_1 x_2 + y_1 y_2 + z_1 z_2)}{r_1 r_2} \quad \text{(B.26)}$$

$$\nabla_1 P_1(12) \cdot \nabla_2 P_1(21) = \frac{\partial P_1(12)}{\partial r_1} \frac{\partial P_1(21)}{\partial r_2} \cos\theta_{12} \quad \text{(B.27)}$$

As in equations (B.23) to (B.27),

$$\nabla_1 P_1(12) \cdot \nabla_2 P_1(21) = \frac{\partial P_1(12)}{\partial r_1} \frac{\partial P_1(21)}{\partial r_2} \cos\theta_{12} \quad \text{(B.28)}$$

and

$$\nabla_2 P_1(12) \cdot \nabla_2 P_1(21) = \frac{\partial P_1(12)}{\partial r_2} \frac{\partial P_1(21)}{\partial r_2} \quad \text{(B.29)}$$

Using equations (B.24), (B.27), (B.28) and (B.29) in (B.22),

$$\nabla_{\bar{r}} P_1(12)\cdot\nabla_{\bar{r}} P_1(21) = \frac{1}{4}\left(\frac{\partial P_1(12)}{\partial r_1}\frac{\partial P_1(21)}{\partial r_1} - \frac{\partial P_1(12)}{\partial r_1}\frac{\partial P_1(21)}{\partial r_2}\cos\theta_{12} - \frac{\partial P_1(21)}{\partial r_1}\frac{\partial P_1(12)}{\partial r_2}\cos\theta_{12} + \frac{\partial P_1(12)}{\partial r_2}\frac{\partial P_1(21)}{\partial r_2}\right) \quad \text{(B.30)}$$

From equation (B.9)

$$\nabla_{\bar{r}}^2 P_1(11) = \frac{1}{4}\nabla_1^2 P_1(11) \quad \text{(B.31)}$$

$$\nabla_1^2 P_1(11) = \frac{\partial^2 P_1(11)}{\partial x_1^2} + \frac{\partial^2 P_1(11)}{\partial y_1^2} + \frac{\partial^2 P_1(11)}{\partial z_1^2} \quad \text{(B.32)}$$

where

$$\frac{\partial^2 P_1(11)}{\partial x_1^2} = \frac{\partial^2 R(11)}{\partial r_1^2}\frac{x_1^2}{r_1^2} + \frac{1}{r_1}\frac{\partial P_1(11)}{\partial r_1} - \frac{x_1}{r_1^3}\frac{\partial P_1(11)}{\partial r_1}$$

$$\frac{\partial^2 P_1(11)}{\partial y_1^2} = \frac{\partial^2 P_1(11)}{\partial r_1^2}\frac{y_1^2}{r_1^2} + \frac{1}{r_1}\frac{\partial P_1(11)}{\partial r_1} - \frac{y_1^2}{r_1^3}\frac{\partial P_1(11)}{\partial r_1}$$

$$\frac{\partial^2 P_1(11)}{\partial z_1^2} = \frac{\partial^2 P_1(11)}{\partial r_1^2}\frac{z_1^2}{r_1^2} + \frac{1}{r_1}\frac{\partial P_1(11)}{\partial r_1} - \frac{z_1^2}{r_1^3}\frac{\partial P_1(11)}{\partial r_1} \quad \text{(B.33)}$$

$$\nabla_1^2 P_1(11) = \frac{\partial^2 P_1(11)}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial P_1(11)}{\partial r_1} \quad \text{(B.34)}$$

$$\nabla_{\bar{r}}^2 P_1(22) = \frac{1}{4}\nabla_2^2 P_1(22) \quad \text{(B.35)}$$

$$\nabla_2^2 P_1(22) = \frac{\partial^2 P_1(22)}{\partial x_2^2} + \frac{\partial^2 P_1(22)}{\partial y_2^2} + \frac{\partial^2 P_1(22)}{\partial z_2^2} \qquad \text{(B.36)}$$

This expression has the same form as equation (B.34), then,

$$\nabla_2^2 P_1(22) = \frac{\partial^2 P_1(22)}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial P_1(22)}{\partial r_2} \qquad \text{(B.37)}$$

$$\nabla_r^2 P_1(12) = \frac{1}{4}\left(\nabla_1^2 P_1(12) + \nabla_2^2 P_1(12) - 2\,\nabla_1 \cdot \nabla_2 P_1(12)\right) \qquad \text{(B.38)}$$

$$\nabla_1 \cdot \nabla_2 P_1(12) = \frac{\partial^2 P_1(12)}{\partial x_1 \partial x_2} + \frac{\partial^2 P_1(12)}{\partial y_1 \partial y_2} + \frac{\partial^2 P_1(12)}{\partial z_1 \partial z_2} \qquad \text{(B.39)}$$

$$\frac{\partial^2 P_1(12)}{\partial x_1 \partial x_2} = \frac{\partial^2 P_1(12)}{\partial r_1 \partial r_2}\frac{x_1}{r_1}\frac{x_2}{r_2}$$

$$\frac{\partial^2 P_1(12)}{\partial y_1 \partial y_2} = \frac{\partial^2 P_1(12)}{\partial r_1 \partial r_2}\frac{y}{r_1}\frac{y}{r_2} \qquad \text{(B.40)}$$

$$\frac{\partial^2 P_1(12)}{\partial z_1 \partial z_2} = \frac{\partial^2 P_1(12)}{\partial r_1 \partial r_2}\frac{z}{r_1}\frac{z}{r_2}$$

$$\nabla_1 \cdot \nabla_2 P_1(12) = \frac{\partial^2 P_1(12)}{\partial r_1 \partial r_2}\frac{(x_1 x_2 + y_1 y_2 + z_1 z_2)}{r_1 r_2} = \frac{\partial^2 P_1(12)}{\partial r_1 \partial r_2}\cos\theta_{12} \qquad \text{(B.41)}$$

According to equations (B.34) and (B.36),

$$\nabla_1^2 P_1(12) = \frac{\partial^2 P_1(12)}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial P_1(12)}{\partial r_1} \tag{B.42}$$

$$\nabla_2^2 P_1(12) = \frac{\partial^2 P_1(12)}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial P_1(12)}{\partial r_2} \tag{B.43}$$

Using equations (B.41) to (B.43) in equation (B.38)

$$\nabla_r^2 P_1(12) = \frac{1}{4}\left(\frac{\partial^2 P_1(12)}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial P_1(12)}{\partial r_1} + \frac{\partial^2 P_1(12)}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial P_1(12)}{\partial r_2} - 2\frac{\partial^2 P_1(12)}{\partial r_1 \partial r_2}\cos\theta_{12}\right) \tag{B.44}$$

and similarly,

$$\nabla_r^2 P_1(21) = \frac{1}{4}\left(\frac{\partial^2 P_1(21)}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial P_1(21)}{\partial r_1} + \frac{\partial^2 P_1(21)}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial P_1(21)}{\partial r_2} - 2\frac{\partial^2 P_1(21)}{\partial r_1 \partial r_2}\cos\theta_{12}\right) \tag{B.45}$$

Equation (B.11) is evaluated at the point $r=0$, or $\bar{r}_1 = \bar{r}_2 = \bar{R}$. Therefore,

$$P_1(11)\Big|_{\bar{r}_1=\bar{R}} = P_1(22)\Big|_{\bar{r}_2=\bar{R}} = P_1(12)\Big|_{\bar{r}_1=\bar{r}_2=\bar{R}} = P_1(21)\Big|_{\bar{r}_1=\bar{r}_2=\bar{R}} = \rho(\bar{R}) \tag{B.46}$$

and the angle between $\bar{r}_1$ and $\bar{r}_2$ becomes zero, so that $\cos\theta_{12} = 1$.

Equation (B.11) is now

$$\nabla^2_{\bar{r}} P_2(1212)\Big|_{\bar{r}=0} = \rho(\bar{R})\ \nabla^2_{\bar{r}} P_1(22)\Big|_{\bar{r}=0} + 2\left(\nabla_{\bar{r}} P_1(11)\cdot\nabla_{\bar{r}} P_1(22)\right)\Big|_{\bar{r}=0} +$$

$$\rho(\bar{R})\ \nabla^2_{\bar{r}} P_1(11)\Big|_{\bar{r}=0} - \frac{1}{2}\ \rho(\bar{R})\,\nabla^2_{\bar{r}} P_1(12)\Big|_{\bar{r}=0} -$$

$$\left(\nabla_{\bar{r}} P_1(12)\cdot\nabla_{\bar{r}} P_1(21)\right)\Big|_{\bar{r}=0} - \frac{1}{2}\rho(\bar{R})\ \nabla^2_{\bar{r}} P_1(21)\Big|_{\bar{r}=0} \qquad \text{(B.47)}$$

From equation (B.19)

$$\left(\nabla_{\bar{r}} P_1(11)\cdot\nabla_{\bar{r}} P_1(21)\right)\Big|_{\bar{r}=0} = \frac{1}{4}\left(\frac{\partial P_1(12)}{\partial r_1}\Big|_{\bar{r}_1=\bar{r}_2=\bar{R}}\ \frac{\partial P_1(21)}{\partial r_1}\Big|_{\bar{r}_1=\bar{r}_2=\bar{R}} - \frac{\partial P_1(12)}{\partial r_1}\Big|_{\bar{r}_1=\bar{r}_2=\bar{R}}\right.$$

$$\frac{\partial P_1(21)}{\partial r_2}\Big|_{\bar{r}_1=\bar{r}_2=\bar{R}} - \frac{\partial P_1(21)}{\partial r_1}\Big|_{\bar{r}_1=\bar{r}_2}\ \frac{\partial P_1(12)}{\partial r_2}\Big|_{\bar{r}_1=\bar{r}_2=\bar{R}} +$$

$$\left.\frac{\partial P_1(12)}{\partial r_2}\Big|_{\bar{r}_1=\bar{r}_2}\ \frac{\partial P_1(21)}{\partial r_2}\Big|_{\bar{r}_1=\bar{r}_2=\bar{R}}\right) \qquad \text{(B.49)}$$

From equations (B.31) and (B.34)

$$\nabla^2_{\bar{r}} P_1(11)\Big|_{\bar{r}=0} = \frac{1}{4}\left(\frac{\partial^2 P_1(11)}{\partial r_1^2}\Big|_{\bar{r}_1=\bar{R}} + \frac{2}{R}\ \frac{\partial P_1(11)}{\partial r_1}\Big|_{\bar{r}_1=\bar{R}}\right. \qquad \text{(B.50)}$$

From equations (B.35) and (B.37)

$$\nabla_{\bar{r}}^2 P_1(22)\Big|_{\bar{r}=0} = \frac{1}{4}\left(\frac{\partial^2 P_1(22)}{\partial r_2^2}\Big|_{\bar{r}_2=\bar{R}} + \frac{2}{R}\frac{\partial P_1(22)}{\partial r_2}\Big|_{\bar{r}_2=\bar{R}}\right) \tag{B.51}$$

From equation (B.44)

$$\nabla_{\bar{r}}^2 P_1(12)\Big|_{\bar{r}=0} = \frac{1}{4}\left(\frac{\partial^2 P_1(12)}{\partial r_1^2} + \frac{2}{R}\frac{\partial P_1(12)}{\partial r_1} + \frac{\partial^2 P_1(12)}{\partial r_2^2} + \frac{2}{R}\frac{\partial P_1(12)}{\partial r_2} - 2\frac{\partial^2 P_1(12)}{\partial r_1 \partial r_2}\right)\Bigg|_{\bar{r}_1=\bar{r}_2=\bar{R}} \tag{B.52}$$

From equation (B.45)

$$\nabla_{\bar{r}}^2 P_1(21)\Big|_{\bar{r}=0} = \frac{1}{4}\left(\frac{\partial^2 P_1(21)}{\partial r_1^2} + \frac{2}{R}\frac{\partial P_1(21)}{\partial r_1} + \frac{\partial^2 P_1(21)}{\partial r_2^2} + \frac{2}{R}\frac{\partial P_1(21)}{\partial r_2} - 2\frac{\partial^2 P_1(21)}{\partial r_1 \partial r_2}\right)\Bigg|_{\bar{r}_1=\bar{r}_2=\bar{R}} \tag{B.53}$$

To evaluate equations (B.47) to (B.53) the first and second derivatives of the different firt-order density matrices are needed.

The first order density matrix has the form

$$P_1(11) = 2\sum_{ij} P_{ij}^{HF}\ \psi_i(1)\ \psi_j(1) \tag{B.54}$$

where P_{ij}^{HF} collects the LCAO coefficients and ψ_i is a Slater type function.

$$\psi_i = \frac{(2\zeta_i)^{n_i+1/2}}{2(\pi(2n_i)!)^{1/2}} \; r^{n_i-1} \exp(-\zeta_i r) \qquad \text{(B.55)}$$

Then

$$\frac{\partial P_1(11)}{\partial r_1} = 2 \sum_{ij} P_{ij}^{HF} \frac{\partial}{\partial r_1}(\psi_i(1)\ \psi_j(1)) =$$

$$2 \sum_{ij} P_{ij}^{HF} \left(\psi_i(1) \frac{\partial \psi_j(1)}{\partial r_1} + \psi_j(1) \frac{\partial \psi_i(1)}{\partial r_1}\right)$$

$$\frac{\partial P_1(22)}{\partial r_2} = 2 \sum_{ij} P_{ij}^{HF} \frac{\partial}{\partial r_2}(\psi_i(2)\ \psi_j(2)) =$$

$$2 \sum_{ij} P_{ij}^{HF} \left(\psi_i(2) \frac{\partial \psi_j(2)}{\partial r_2} + \psi_j(2) \frac{\partial \psi_i(2)}{\partial r_2}\right)$$

$$\frac{\partial P_1(12)}{\partial r_1} = 2 \sum_{ij} P_{ij}^{HF} \frac{\partial \psi_i(1)}{\partial r_1}\ \psi_j(2) \qquad \text{(B.56)}$$

$$\frac{\partial P_1(12)}{\partial r_2} = 2 \sum_{ij} P_{ij}^{HF}\ \psi_i(1)\ \frac{\partial \psi_j(2)}{\partial r_2}$$

$$\frac{\partial P_1(21)}{\partial r_1} = 2 \sum_{ij} P_{ij}^{HF}\ \psi_i(2) \frac{\partial \psi_j(1)}{\partial r_1}$$

$$\frac{\partial P_1(21)}{\partial r_2} = 2 \sum_{ij} P_{ij}^{HF} \frac{\partial \psi_i(2)}{\partial r_2} \psi_j(1)$$

$$\frac{\partial^2 P_1(11)}{\partial r_1^2} = 2 \sum_{ij} P_{ij}^{HF} \left(\psi_i(1) \frac{\partial^2 \psi_j(1)}{\partial r_1^2} + 2 \frac{\partial \psi_i(1)}{\partial r_1} \frac{\partial \psi_j(1)}{\partial r_1} + \psi_j(1) \frac{\partial^2 \psi_i(1)}{\partial r_1^2} \right)$$

$$\frac{\partial^2 P_1(22)}{\partial r_2^2} = 2 \sum_{ij} P_{ij}^{HF} \left(\psi_i(2) \frac{\partial^2 \psi_j(2)}{\partial r_2^2} + 2 \frac{\partial \psi_i(2)}{\partial r_2} \frac{\partial \psi_j(2)}{\partial r_2} + \psi_j(2) \frac{\partial^2 \psi_i(2)}{\partial r_2^2} \right)$$

$$\frac{\partial^2 P_1(12)}{\partial r_1^2} = 2 \sum_{ij} P_{ij}^{HF} \frac{\partial^2 \psi_i(1)}{\partial r_1^2} \psi_j(2)$$

$$\frac{\partial^2 P_1(12)}{\partial r_2^2} = 2 \sum_{ij} P_{ij}^{HF} \psi_i(1) \frac{\partial^2 \psi_j(2)}{\partial r_2^2} \qquad \text{(B.57)}$$

$$\frac{\partial^2 P_1(12)}{\partial r_1 \partial r_2} = 2 \sum_{ij} P_{ij}^{HF} \frac{\partial \psi_i(1)}{\partial r_1} \frac{\partial \psi_j(2)}{\partial r_2}$$

$$\frac{\partial^2 P_1(21)}{\partial r_1^2} = 2 \sum_{ij} P_{ij}^{HF} \psi_i(2) \frac{\partial^2 \psi_j(1)}{\partial r_1^2}$$

$$\frac{\partial^2 P_1(21)}{\partial r_2^2} = 2 \sum_{ij} P_{ij}^{HF} \frac{\partial^2 \psi_i(2)}{\partial r_2^2} \psi_j(1)$$

$$\frac{\partial^2 P_1(21)}{\partial r_1 \partial r_2} = 2 \sum_{ij} P_{ij}^{HF} \frac{\partial \psi_i(2)}{\partial r_2} \frac{\partial \psi_j(1)}{\partial r_1}$$

The derivatives of the basis functions are

$$\frac{\partial \psi_i(1)}{\partial r_1} = c_i (n_i - 1) r_1^{n_i - 2} \exp(-\xi_i r_1) - c_i \xi_i r_1^{n_i - 1} \exp(-\xi_i r_1) \quad \text{(B.58)}$$

$$\text{where} \quad c_i \equiv \frac{(2\xi_i)^{n_i + 1/2}}{2(\pi (2n_i)!)^{1/2}} \quad \text{(B.59)}$$

$$\frac{\partial \psi_i(1)}{\partial r_1} = ((n_i - 1) r_1^{-1} - \xi_i) \psi_i(1) \quad \text{(B.60)}$$

$$\left.\frac{\partial \psi_i(1)}{\partial r_1}\right|_{\bar{r}_1 = \bar{R}} = \left.\frac{\partial \psi_i(2)}{\partial r_2}\right|_{\bar{r}_2 = \bar{R}} = ((n_i - 1) R^{-1} - \xi_i) \psi_i(\bar{R}) \quad \text{(B.61)}$$

$$\frac{\partial^2 \psi_i(1)}{\partial r_1^2} = ((n_i - 1)(n_i - 2) r_1^{-2} - 2\xi_i (n_i - 1) r_1^{-1} + \xi_i^2) \psi_i(1) \quad \text{(B.62)}$$

$$\left.\frac{\partial^2 \psi_i(1)}{\partial r_1^2}\right|_{\bar{r}=0} = \left.\frac{\partial^2 \psi_i(2)}{\partial r_2^2}\right|_{r=0} = ((n_i - 1)(n_i - 2) R^{-2} - 2\xi_i (n_i - 1) R^{-1} + \xi_i^2) \psi_i(\bar{R}) \quad \text{(B.63)}$$

Combining equations (B.55) to (B.64) with (B.48) to (B.53)

$$\left(\nabla_{\vec{r}} P_1(11) \cdot \nabla_{\vec{r}} P_1(22)\right)\Big|_{\vec{r}=0} = -\frac{1}{4}\left[2 \sum_{ij} P_{ij}^{HF} \left((n_i+n_j-2)\, R^{-1} - (\xi_i+\xi_j)\right) \psi_i(R)\ \psi_j(R)\right]^2 \tag{B.64}$$

$$\left(\nabla_{\vec{r}} P_1(12) \cdot \nabla_{\vec{r}} P_1(21)\right)\Big|_{\vec{r}=0} = -\frac{1}{4}\left[2 \sum_{ij} P_{ij}^{HF} \left((n_i-n_j)\, R^{-1} - (\xi_i-\xi_j)\right) \psi_i(R)\ \psi_j(R)\right]^2 \tag{B.65}$$

$$\nabla_{\vec{r}}^2 P_1(11)\Big|_{r=0} = \frac{1}{4}\, 2 \sum_{ij} P_{ij}^{HF} \left((n_i+n_j-2)^2\, R^{-2} + (n_i+n_j-2)\, R^{-2} - 2\,(\xi_i+\xi_j)\,(n_i+n_j-1)\, R^{-1} + (\xi_i+\xi_j)^2\right) \psi_i(R)\ \psi_j(R) \tag{B.66}$$

$$\nabla_{\vec{r}}^2 P_1(22)\Big|_{r=0} = \nabla_{\vec{r}}^2 P_1(11)\Big|_{r=0} \tag{B.67}$$

$$\nabla_r^2 P_1(12)\Big|_{r=0} = \frac{1}{4}\, 2 \sum_{ij} P_{ij}^{HF} \left((n_i - n_j)^2 R^{-2} + (n_i + n_j - 2) R^{-2} - 2 (\xi_i - \xi_j)(n_i - n_j) R^{-1} - 2 (\xi_i + \xi_j) R^{-1} + (\xi_i - \xi_j)^2\right) \psi_i(R)\, \psi_j(R) \tag{B.68}$$

$$\nabla_r^2 P_1(21)\Big|_{r=0} = \nabla_r^2 P_1(12)\Big|_{r=0} \tag{B.69}$$

Using equations (B.64) to (B.69) in equation (B.47)

$$\nabla_r^2 P_2(1212)\Big|_{r=0} = \rho(R) \sum_{ij} P_{ij}^{HF} \left((n_i + n_j - 2)^2 R^{-2} + (n_i + n_j - 2) R^{-2} - 2 (\xi_i + \xi_j)(n_i + n_j - 1) R^{-1} + (\xi_i + \xi_j)^2\right) \psi_i(R)\, \psi_j(R) - 2 \left[\sum_{ij} P_{ij}^{HF} \left((n_i + n_j - 2) R^{-1} - (\xi_i + \xi_j)\right) \psi_i(R)\, \psi_j(R)\right]^2 - \frac{1}{2} \rho(R) \sum_{ij} P_{ij}^{HF} \left((n_i - n_j)^2 R^{-2} + (n_i + n_j - 2) R^{-2} - 2 (\xi_i - \xi_j)(n_i - n_j) R^{-1} - 2 (\xi_i + \xi_j) R^{-1} + (\xi_i - \xi_j)^2\right) \psi_i(R)\, \psi_j(R) + \left[\sum_{ij} P_{ij}^{HF} \left((n_i - n_j) R^{-1} - (\xi_i - \xi_j)\right) \psi_i(R)\, \psi_j(R)\right]^2 \tag{B.70}$$

APPENDIX C

Correlation Energy Formalism

In addition to equations (B.1) to (B.10), the following relationships and integrals will be used in this appendix, from equations (B.3) to (B.5):

$$\frac{\partial R}{\partial x_1} = \frac{X}{R} = \frac{(x_1+x_2)}{2R}$$

$$\frac{\partial R}{\partial y_1} = \frac{Y}{R} = \frac{(y_1+y_2)}{2R} \qquad \text{(C.1)}$$

$$\frac{\partial R}{\partial z_1} = \frac{Z}{R} = \frac{(z_1+z_2)}{2R}$$

$$\frac{\partial r}{\partial x_1} = \frac{x}{r} = \frac{(x_1-x_2)}{r}$$

$$\frac{\partial r}{\partial y_1} = \frac{y}{r} = \frac{(y_1-y_2)}{r} \qquad \text{(C.2)}$$

$$\frac{\partial r}{\partial z_1} = \frac{z}{r} = \frac{(z_1-z_2)}{r}$$

To change the variables of integration from $\bar{r}_1, \bar{r}_2$ to $\bar{r}, \bar{R}$ the Jacobian determinant is needed,

$$\frac{\partial(\bar{r}_1, \bar{r}_2)}{\partial(\bar{r}, \bar{R})} = \begin{vmatrix} 1 & -1 \\ 1 & 1 \end{vmatrix} = 1 \qquad (C.3)$$

The integrals of the various exponenetials over r are,

$$\int_0^\infty x^n \exp(-q\,x)\,dx = \frac{n!}{q^{n+1}} \qquad n > -1,\ q > 0$$

$$\int_0^\infty \exp(-b\,x^2)\,dx = \frac{1}{2}\left(\frac{\pi}{b}\right)^{1/2}$$

$$\int_0^\infty x^{2n} \exp(-b\,x^2)\,dx = \frac{1\cdot 3\cdots(2n-1)}{2^{n+1}}\left(\frac{\pi}{b^{2n+1}}\right)^{1/2} \quad n=1,2,3\ldots$$

$$\int_0^\infty \exp(-\beta^2 r^2)\,dr = \frac{1}{2}\frac{\sqrt{\pi}}{\beta}$$

$$\int_0^\infty \exp(-\beta^2 r^2)\,r\,dr = \frac{1}{2\beta}$$

$$\int_0^\infty \exp(-\beta^2 r^2)\,r^2\,dr = \frac{1}{4}\frac{\sqrt{\pi}}{\beta^3}$$

$$\int_0^\infty \exp(-\beta^2 r^2)\ r^3\ dr = \frac{1}{2\beta^4}$$

$$\int_0^\infty \exp(-\beta^2 r^2)\ r^4\ dr = \frac{3}{8}\ \frac{\sqrt{\pi}}{\beta^5} \qquad \text{(C.4)}$$

$$\int_0^\infty \exp(-\beta^2 r^2)\ r^5\ dr = \frac{1}{\beta^6}$$

$$\int_0^\infty \exp(-\beta^2 r^2)\ r^6\ dr = \frac{15}{16}\ \frac{\sqrt{\pi}}{\beta^7}$$

$$\int_0^\infty \exp(-\beta^2 r^2)\ r^7\ dr = \frac{3}{\beta^8}$$

$$\int_0^\infty \exp(-\beta^2 r^2)\ r^8\ dr = \frac{105}{32}\ \frac{\sqrt{\pi}}{\beta^9}$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ dr = \frac{1}{2\beta}\sqrt{\frac{\pi}{2}}$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ r\ dr = \frac{1}{4\beta^2}$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ r^2\ dr = \frac{1}{8\beta^3}\sqrt{\frac{\pi}{2}}$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ r^3\ dr = \frac{1}{8\beta^4}$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ r^4\ dr = \frac{3}{32\beta^5}\sqrt{\frac{\pi}{2}}$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ r^5\ dr = \frac{1}{8\beta^6} \qquad \text{(C.5)}$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ r^6\ dr = \frac{15}{128\beta^7}\sqrt{\frac{\pi}{2}}$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ r^7\ dr = \frac{3}{16\beta^8}$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ r^8\ dr = \frac{105}{512\beta^9}\sqrt{\frac{\pi}{2}}$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ r^9\ dr = \frac{3}{8\beta^{10}}$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ r^{10}\ dr = \frac{945}{2048\beta^{11}}\sqrt{\frac{\pi}{2}}$$

Calculation of Vc

$$Vc = \frac{1}{2}\int P_{2\underline{det}}(1212)\ b(1212)\frac{1}{|\bar{r}_1 - \bar{r}_2|}\,d\bar{r}_1\ d\bar{r}_2 \qquad (C.6)$$

Change of variables according to (B.1)

$$Vc = \frac{1}{2}\int P_{2\underline{det}}(1212)\ b(1212)\ \frac{d\bar{r}}{r}\,d\bar{R} \qquad (C.7)$$

$P_{2\underline{det}}(1212)$ is expanded in a Taylor series ut $\bar{r}=0$. Only the leading term is retained,

$$P_{2\underline{det}}(1212)\Big|_{\bar{r}=0} = \frac{1}{2}\rho^2(\bar{R}) \qquad (C.8)$$

Thus

$$Vc = \frac{1}{4}\int d\bar{R}\ \rho^2(\bar{R})\ \int d\bar{r}\ \frac{(\varphi^2(12) - 2\,\varphi(12))}{r} \qquad (C.9)$$

where

$$\varphi(12) = (1-\Phi(\bar{R}))\ \exp(-\beta^2 r^2) - \frac{\Phi}{2}(\bar{R})\ r\ \exp(-\beta^2 r^2) \qquad (C.10)$$

$$Vc = \pi \int d\bar{R}\ \rho^2(\bar{R})\ [(1-\Phi)^2 \int_0^\infty \exp(-2\beta^2 r^2)\ r\ dr - (1-\Phi)\ \Phi$$

$$\int_0^\infty \exp(-2\beta^2 r^2)\ r^2\ dr + \frac{\Phi^2}{4} \int_0^\infty \exp(-2\beta^2 r^2)\ r^3\ dr - 2$$

$$(1-\Phi) \int_0^\infty \exp(-\beta^2 r^2)\ r\ dr + \Phi \int_0^\infty \exp(-\beta^2 r^2)\ r^2\ dr] \qquad (C.11)$$

Using the integrals (C.4) and (C.5),

$$Vc = \pi \int d\bar{R}\ \rho^2(\bar{R}) \left[\frac{(1-\Phi)^2}{4\beta^2} + \frac{\Phi(\Phi-1)}{8\beta^3}\sqrt{\frac{\pi}{2}} + \frac{\Phi^2}{32\beta^4} - \frac{(1-\Phi)}{\beta^2} + \frac{\sqrt{\pi}\ \Phi}{4\beta^3}\right] \qquad (C.12)$$

For the systems studied in Chapter 3 there is not angular dependence, only s-type orbitals are involved. Then,

$$Vc = 4\pi^2 \int_0^\infty \rho^2(R) \left(\frac{(1-\Phi)^2}{4\beta^2} + \frac{\Phi(\Phi-1)}{8\beta^3}\sqrt{\frac{\pi}{2}} + \frac{\Phi}{32\beta^4} - \frac{(1-\Phi)}{\beta^2} + \frac{\sqrt{\pi}\ \Phi}{4\beta^3}\right) R^2\ dR \qquad (C.13)$$

This integral is evaluated numerically by using the trapezoidal rule. The upper limit of integration is the smallest value of R necessary for convergence.

Calculation of Tc

$$Tc = -\frac{1}{2}\int \nabla_1^2 (P_{2\underline{det}}(121'2)\ b(121'2))\Big|_{1'\to 1}\ d\bar{r}_1\ d\bar{r}_2 \qquad (C.14)$$

Change of variables according to (B.1)

$$Tc = -\frac{1}{2}\Big[\iint d\bar{r}\ d\bar{R}\ P_{2\underline{det}}(1212)\ \nabla_1^2 b(121'2)\Big|_{1'\to 1} + 2\int d\bar{r}\ d\bar{R}$$

$$(\nabla_1 P_{2\underline{det}}(121'2)\cdot \nabla_1 b(121'2))\Big|_{1'\to 1} + \int d\bar{r}\ d\bar{R}$$

$$\nabla_1^2 P_{2\underline{det}}(121'2)\Big|_{1'\to 1}\ b(1212)\Big] \qquad (C.15)$$

$$Tc_1 \equiv \int d\bar{r}\ d\bar{R}\ P_{2\underline{det}}(1212)\ \nabla_1^2 b(121'2)\Big|_{1'\to 1} \qquad (C.16)$$

Taylor-series expansion of $P_{2\underline{det}}$ about $\bar{r}=0$ retaining only the leading term gives

$$Tc_1 = \frac{1}{2}\int d\bar{R}\ \rho^2(\bar{R})\ \int d\bar{r}\ \nabla_1^2 b(121'2)\Big|_{1'\to 1} \qquad (C.17)$$

where

$$\nabla_1^2 b(121'2)\Big|_{1'\to 1} = -\ \varphi(12)\ \nabla_1^2\varphi(12) + \nabla_1^2\varphi(12) \qquad (C.18)$$

Using the chain rule and the relationships (B.1) to (B.10) and (C.1) to (C.2)

$$\nabla_1^2 \psi(12) = \frac{\partial^2 \psi(12)}{\partial x_1^2} + \frac{\partial^2 \psi(12)}{\partial y_1^2} + \frac{\partial^2 \psi(12)}{\partial z_1^2} \qquad \text{(C.19)}$$

$$\frac{\partial^2 \psi(12)}{\partial x_1^2} = \frac{\partial}{\partial x_1}\left(\frac{\partial \psi(12)}{\partial R}\frac{\partial R}{\partial x_1} + \frac{\partial \psi(12)}{\partial r}\frac{\partial r}{\partial x_1}\right) \qquad \text{(C.20)}$$

$$\begin{aligned}\frac{\partial^2 \psi(12)}{\partial x_1^2} = {} & \frac{1}{4R^2}\frac{\partial^2 \psi(12)}{\partial R^2}\frac{(x_1+x_2)^2}{4} + \frac{1}{4R}\frac{\partial \psi(12)}{\partial R} - \frac{1}{4R^3}\\ & \frac{\partial \psi(12)}{\partial R}\frac{(x_1+x_2)^2}{4} + \frac{1}{r^2}\frac{\partial^2 \psi(12)}{\partial r^2}(x_1-x_2)^2 + \frac{1}{r}\\ & \frac{\partial \psi(12)}{\partial r} - \frac{1}{r^3}\frac{\partial \psi(12)}{\partial r}(x_1-x_2)^2 + \frac{1}{rR}\frac{\partial^2 \psi(12)}{\partial R \partial r}\\ & (x_1-x_2)\frac{(x_1+x_2)}{2}\end{aligned} \qquad \text{(C.21)}$$

The form of $\partial^2\psi(12)/\partial y_1^2$ and of $\partial^2\psi(12)/\partial z_1^2$ are analogous to the form of $\partial^2\psi(12)/\partial x_1^2$, then

$$\nabla_1^2\varphi(12) = \frac{1}{4R^2}\frac{\partial^2\varphi(12)}{\partial R^2}\left(\frac{(x_1+x_2)^2}{4} + \frac{(y_1+y_2)^2}{4} + \frac{(z_1+z_2)^2}{4}\right)$$

$$+ \frac{3}{4R}\frac{\partial\varphi(12)}{\partial R} - \frac{1}{4R^3}\frac{\partial\varphi(12)}{\partial R}\left(\frac{(x_1+x_2)^2}{4} + \frac{(y_1+y_2)^2}{4}\right.$$

$$\left. + \frac{(z_1+z_2)^2}{4}\right) + \frac{1}{r^2}\frac{\partial^2\varphi(12)}{\partial r^2}\left((x_1-x_2)^2 + (y_1-y_2)^2\right.$$

$$\left. + (z_1-z_2)^2\right) + \frac{3}{r}\frac{\partial\varphi(12)}{\partial r} - \frac{1}{r^3}\frac{\partial\varphi(12)}{\partial r}\left((x_1-x_2)^2 +\right.$$

$$\left. + (y_1-y_2)^2 + (z_1-z_2)^2\right) + \frac{1}{rR}\frac{\partial^2\varphi(12)}{\partial R\partial r}\left((x_1-x_2)\right.$$

$$\left.\frac{(x_1+x_2)}{2} + (y_1-y_2)\frac{(y_1+y_2)}{2} + (z_1-z_2)\frac{(z_1+z_2)}{2}\right) \qquad \text{(C.22)}$$

$$\nabla_1^2\varphi(12) = \frac{1}{4}\frac{\partial^2\varphi(12)}{\partial R^2} + \frac{1}{2R}\frac{\partial\varphi(12)}{\partial R} + \frac{\partial^2\varphi(12)}{\partial r^2} + \frac{2}{r}\frac{\partial\varphi(12)}{\partial r}$$

$$+ \frac{\partial^2\varphi(12)}{\partial R\partial r}\cos\theta \qquad \text{(C.23)}$$

$$\frac{\partial\varphi(12)}{\partial R} = -2\beta\frac{d\beta}{dR}r^2\,e^{-\beta^2r^2} - \frac{d\Phi}{dR}e^{-\beta^2r^2} + 2\beta\frac{d\beta}{dR}r^2\,\Phi\,e^{-\beta^2r^2} - \frac{1}{2}$$

$$\frac{d\Phi}{dR}r\,e^{-\beta^2r^2} + \beta\frac{d\beta}{dR}\Phi\,r^3\,e^{-\beta^2r^2} \qquad \text{(C.24)}$$

$$\frac{\partial\varphi(12)}{\partial r} = -2\beta^2 r\,(1-\Phi)\,e^{-\beta^2r^2} - \frac{\Phi}{2}e^{-\beta^2r^2} + \Phi\beta^2 r^2\,e^{-\beta^2r^2} \qquad \text{(C.25)}$$

$$\frac{\partial^2\varphi(12)}{\partial R^2} = -2\left(\frac{d\beta}{dR}\right)^2 r^2\, e^{-\beta^2 r^2} - 2\beta\frac{d^2\beta}{dR^2} r^2\, e^{-\beta^2 r^2} + 4\beta^2\left(\frac{d\beta}{dR}\right)^2 r^4\, e^{-\beta^2 r^2}$$

$$- \frac{d^2\Phi}{dR^2} e^{-\beta^2 r^2} + 2\beta\frac{d\beta}{dR}\frac{d\Phi}{dR} r^2\, e^{-\beta^2 r^2} + 2\left(\frac{d\beta}{dR}\right)^2 r^2\,\Phi\, e^{-\beta^2 r^2}$$

$$+ 2\beta\frac{d^2\beta}{dR^2} r^2\,\Phi\, e^{-\beta^2 r^2} + 2\beta\frac{d\beta}{dR} r^2\frac{d\Phi}{dR} e^{-\beta^2 r^2} - 4\beta^2\left(\frac{d\beta}{dR}\right)^2$$

$$r^4\,\Phi\, e^{-\beta^2 r^2} - \frac{1}{2}\frac{d^2\Phi}{dR^2} r\, e^{-\beta^2 r^2} + \beta\frac{d\beta}{dR}\frac{d\Phi}{dR} r^3\, e^{-\beta^2 r^2} + \left(\frac{d\beta}{dR}\right)^2$$

$$\Phi\, r^3\, e^{-\beta^2 r^2} + \beta\frac{d^2\beta}{dR^2}\,\Phi\, r^3\, e^{-\beta^2 r^2} + \beta\frac{d\beta}{dR}\frac{d\Phi}{dR} r^3\, e^{-\beta^2 r^2} - 2$$

$$\beta^2\left(\frac{d\beta}{dR}\right)^2\Phi\, r^5\, e^{-\beta^2 r^2} \qquad \text{(C.26)}$$

$$\frac{\partial^2\varphi(12)}{\partial r^2} = -2\beta^2\,(1-\Phi)\, e^{-\beta^2 r^2} + 4\beta^4\, r^2\,(1-\Phi)\, e^{-\beta^2 r^2} + \Phi\beta^2\, r\, e^{-\beta^2 r^2} +$$

$$2\,\Phi\,\beta^2 r\, e^{-\beta^2 r^2} - 2\,\Phi\,\beta^4 r^3\, e^{-\beta^2 r^2} \qquad \text{(C.27)}$$

Using equations (C.24) to (C.27) in equation (C.23)

$$\nabla_1^2\varphi(12) = -\frac{\Phi}{r}e^{-\beta^2r^2}-\left(\frac{1}{2R}\frac{d\Phi}{dR}+\frac{1}{4}\frac{d^2\Phi}{dR^2}+6\beta^2(1-\Phi)\right)e^{-\beta^2r^2}+$$

$$\left(\frac{-1}{8}\frac{d^2\Phi}{dR^2}-\frac{1}{4R}\frac{d\Phi}{dR}+5\Phi\beta^2\right)r\,e^{-\beta^2r^2}+\left(\beta\frac{(\Phi-1)}{2}\frac{d^2\beta}{dR^2}+\right.$$

$$\beta\frac{(\Phi-1)}{R}\frac{d\beta}{dR}+\frac{(\Phi-1)}{2}\left(\frac{d\beta}{dR}\right)^2+\beta\frac{d\beta}{dR}\frac{d\Phi}{dR}+4\beta^4(1-\Phi)$$

$$r^2e^{-\beta^2r^2}+\left(\frac{\Phi}{4}\beta\frac{d^2\beta}{dR^2}+\frac{\Phi\beta}{2R}\frac{d\beta}{dR}+\frac{\Phi}{4}\left(\frac{d\beta}{dR}\right)^2+\frac{\beta}{2}\frac{d\beta}{dR}\right.$$
$$\left.\frac{d\Phi}{dR}-2\beta^4\Phi\right)r^3e^{-\beta^2r^2}+\beta^2\left(\frac{d\beta}{dR}\right)^2(1-\Phi)\,r^4\,e^{-\beta^2r^2}-$$

$$\frac{\Phi}{2}\beta^2\left(\frac{d\beta}{dR}\right)^2r^5e^{-\beta^2r^2}+\frac{\partial^2\varphi(12)}{\partial R\,\partial r}\cos\theta \qquad (C.28)$$

$$I_1 \equiv \int\nabla_1^2\varphi(12)\,d\bar{r}$$

Using integrals (C.4) and (C.5)

$$I_1 = 4\pi\left[\frac{-\Phi}{2\beta^2}+\frac{\sqrt{\pi}}{4\beta^3}\left(6\beta^2(\Phi-1)-\frac{1}{4}\frac{d^2\Phi}{dR^2}-\frac{1}{2R}\frac{d\Phi}{dR}\right)+\right.$$

$$\frac{1}{2\beta^4}\left(5\beta^2\Phi-\frac{1}{8}\frac{d^2\Phi}{dR^2}-\frac{1}{4R}\frac{d\Phi}{dR}\right)+\frac{3}{8}\frac{\sqrt{\pi}}{\beta^5}\left(\beta\frac{d\beta}{dR}\frac{d\Phi}{dR}\right.$$

$$+\frac{(\Phi-1)}{2}\left(\frac{d\beta}{dR}\right)^2+\beta\frac{(\Phi-1)}{2}\frac{d^2\beta}{dR^2}+\beta\frac{(\Phi-1)}{R}\frac{d\beta}{dR}-4$$

$$\left.\beta^4(\Phi-1)\right)+\frac{1}{\beta^6}\left(\frac{\Phi}{4}\beta\frac{d^2\beta}{dR^2}+\frac{\Phi}{2R}\beta\frac{d\beta}{dR}+\frac{\beta}{2}\frac{d\beta}{dR}\frac{d\Phi}{dR}+\right.$$

$$\frac{\Phi}{4}\left(\frac{d\beta}{dR}\right)^2-2\beta^4\Phi\Big)-\frac{15\sqrt{\pi}}{16\beta^5}(\Phi-1)\left(\frac{d\beta}{dR}\right)^2-\frac{3}{2}\frac{\Phi}{\beta^5}$$

$$\left.\left(\frac{d\beta}{dR}\right)^2\right] \qquad (C.29)$$

The last term in equation (C.28) vanishes upon integration

$$\int_0^{2\pi} d\varphi \int_0^{\infty} r^2\, dr\, \frac{\partial \varphi^2(12)}{\partial R\, \partial r} \int_0^{\pi} \cos\theta \sin\theta\, d\theta = 0$$

Using equations (C.10) and (C.28)

$$\varphi(12)\, \nabla_1^2\, \varphi(12) = \frac{\Phi}{r}(\Phi-1)\, e^{-2\beta^2 r^2} + \left(\frac{\Phi}{2} + \frac{(\Phi-1)}{4}\frac{d^2\Phi}{dR^2} + \frac{d\Phi}{dR}\right.$$

$$\frac{(\Phi-1)}{2R} - 6\beta^2(\Phi-1)^2\Big)\, e^{-2\beta^2 r^2} + \left(\frac{\Phi}{16}\frac{d^2\Phi}{dR^2} + \frac{\Phi}{8R}\frac{d\Phi}{dR}\right.$$

$$\frac{5}{2}\beta^2\Phi^2 - \frac{\beta}{2}(\Phi-1)^2\frac{d^2\beta}{dR^2} - \frac{\beta}{R}(\Phi-1)^2\frac{d\beta}{dR} - \frac{(\Phi-1)^2}{2}$$

$$\left(\frac{d\beta}{dR}\right)^2 + (1-\Phi)\left(\beta\frac{d\beta}{dR}\frac{d\Phi}{dR} + 4\beta^4(1-\Phi)^2\right)\, r^2\, e^{-2\beta^2 r^2} +$$

$$\frac{\Phi}{8}\frac{d^2\Phi}{dR^2} + \frac{\Phi}{4R}\frac{d\Phi}{dR} + 3\Phi\beta^2(1-\Phi) - \frac{(1-\Phi)}{8}\frac{d^2\Phi}{dR^2} -$$

$$\frac{(1-\Phi)}{4R}\frac{d\Phi}{dR} + 5\beta^2\Phi(1-\Phi)\Big)\, r\, e^{-2\beta^2 r^2} + \left(\frac{(1-\Phi)}{2}\beta\Phi\frac{d^2\beta}{dR^2}\right.$$

$$+ \frac{(1-\Phi)}{R}\Phi\beta\frac{d\beta}{dR} + \frac{(1-\Phi)}{2}\Phi\left(\frac{d\beta}{dR}\right)^2 + \frac{(1-2\Phi)}{2}\beta\frac{d\beta}{dR}$$

$$\frac{d\Phi}{dR} - 4\beta^4\Phi(1-\Phi)\Big)\, r^3\, e^{-2\beta^2 r^2} + \left((1-\Phi)^2\beta^2\left(\frac{d\beta}{dR}\right)^2 - \frac{\Phi^2}{8}\right.$$

$$\beta\frac{d^2\beta}{dR^2} - \frac{\Phi^2}{4R}\beta\frac{d\beta}{dR} - \frac{\Phi^2}{8}\left(\frac{d\beta}{dR}\right)^2 - \frac{\beta}{4}\Phi\frac{d\beta}{dR}\frac{d\Phi}{dR} + \beta^4\Phi^2\Big)$$

$$r^4 e^{-2\beta^2 r^2} - \Phi \beta^2 \left(\frac{d\beta}{dR}\right)^2 (1-\Phi) r^5 e^{-2\beta^2 r^2} + \frac{\Phi^2}{4} \beta^2 \left(\frac{d\beta}{dR}\right)^2 r^6$$

$$e^{-2\beta^2 r^2} + \varphi(12) \frac{\partial^2 \varphi(12)}{\partial R \partial r} \cos\theta \qquad \text{(C.30)}$$

$$I_2 \equiv \int \varphi(12) \nabla_1^2 \varphi(12) \, d\bar{r}$$

Using integrals (C.4) and (C.5)

$$I_2 = 4\pi \Big[\frac{\Phi(\Phi-1)}{4\beta^2} + \frac{1}{8\beta^3}\sqrt{\frac{\pi}{2}} \Big(\frac{(\Phi-1)}{4} \frac{d^2\Phi}{dR^2} + \frac{(\Phi-1)}{2R} \frac{d\Phi}{dR} - 6\beta^2 (\Phi-1)^2 + \frac{\Phi^2}{2} \Big) + \frac{1}{32\beta^4} \Big(\frac{(2\Phi-1)}{8} \frac{d^2\Phi}{dR^2} + \frac{(2\Phi-1)}{4R} \frac{d\Phi}{dR} + 8\Phi \beta^2(1-\Phi) \Big) + \frac{3}{32\beta^5}\sqrt{\frac{\pi}{2}} \Big((1-\Phi)\beta \frac{d\beta}{dR} \frac{d\Phi}{dR} - \frac{(\Phi-1)^2}{2} \left(\frac{d\beta}{dR}\right)^2 - \frac{(\Phi-1)^2}{2} \beta \frac{d^2\beta}{dR^2} - \frac{(\Phi-1)}{R} \beta \frac{d\beta}{dR} + 4\beta^4 (1-\Phi)^2 + \frac{\Phi}{16} \frac{d^2\Phi}{dR^2} + \frac{\Phi}{8R} \frac{d\Phi}{dR} - \frac{5}{2} \beta^2 \Phi^2 \Big) + \frac{1}{8\beta^6} \frac{(1-2\Phi)}{2} \beta \frac{d\beta}{dR} \frac{d\Phi}{dR} + \frac{(1-\Phi)}{2} \Phi \left(\frac{d\beta}{dR}\right)^2 + \frac{(1-\Phi)}{2} \Phi \beta \frac{d^2\beta}{dR^2} + \frac{(1-\Phi)}{R} \Phi \beta \frac{d\beta}{dR} + 4\beta^4 \Phi(\Phi-1) \Big) + \frac{15}{128\beta^7}\sqrt{\frac{\pi}{2}} \Big((1-\Phi)^2 \beta^2 \left(\frac{d\beta}{dR}\right)^2 - \frac{\Phi^2}{8} \left(\frac{d\beta}{dR}\right)^2 - \frac{\Phi}{4} \beta \frac{d\beta}{dR} \frac{d\Phi}{dR} - \frac{\Phi^2}{8} \beta \frac{d^2\beta}{dR^2} - \frac{\Phi^2}{4R} \beta \frac{d\beta}{dR} + \beta^4 \Phi^2 \Big) + \frac{3\Phi(\Phi-1)}{16\beta^6} \left(\frac{d\beta}{dR}\right)^2 + \frac{\Phi^2}{4\beta^7} \left(\frac{d\beta}{dR}\right)^2 \Big]$$

$$(105/512)(\pi/2)^{1/2} \qquad \text{(C.31)}$$

Combining equations (C.17), (C.18), (C.29) and (C.31)

$$Tc_1 = 2 \int_o^\infty R^2 \, \rho^2(\bar{R}) \, (-I_1 + I_2) \, dR \tag{C.32}$$

$$Tc_2 = \int d\bar{r} \, d\bar{R} \, (\nabla_1 P_{2\underline{det}}(121'2) \cdot \nabla_1 b(121'2))\Big|_{1'\to 1} \tag{C.33}$$

According to equations (B.7)

$$\nabla_1 P_{2\underline{det}}(121'2)\Big|_{1'\to 1} = \frac{\partial P_{2\underline{det}}(121'2)}{\partial x_1}\Big|_{1'\to 1} \hat{i} + \frac{\partial P_{2\underline{det}}(121'2)}{\partial y_1}\Big|_{1'\to 1} \hat{j} + \frac{\partial P_{2\underline{det}}(121'2)}{\partial z_1}\Big|_{1'\to 1} \hat{k} \tag{C.34}$$

and

$$\nabla_1 b(121'2)\Big|_{1'\to 1} = \frac{\partial b(121'2)}{\partial x_1}\Big|_{1'\to 1} \hat{i} + \frac{\partial b(121'2)}{\partial y_1}\Big|_{1'\to 1} \hat{j} + \frac{\partial b(121'2)}{\partial z_1}\Big|_{1'\to 1} \hat{k} \tag{C.35}$$

The vector $\nabla_1 P_{2\underline{det}}(121'2)\Big|_{1'\to 1}$ is expanded in a Taylor series about $\bar{r}=0$ up to zeroth order. Usin the relationships (B.3) to (B.5), (B.10) and (C.1) to (C.2),

$$\nabla_1 P_{2\underline{det}}(121'2)\Big|_{1'\to 1} = \bar{V}(X,Y,Z,x,y,z)$$

$$\bar{V}(X,Y,Z,x,y,z,) \cong \bar{V}(X,Y,Z,0,0,0) \qquad (C.36)$$

$$\bar{V}(X,Y,Z,0,0,0) = \frac{\partial P_{2\underline{det}}(121'2)}{\partial x_1}\Big|_{\substack{1'\to 1\\ r=0}} \hat{i} + \frac{\partial P_{2\underline{det}}(121'2)}{\partial y_1}\Big|_{\substack{1'\to i\\ r=0}} \hat{j}$$

$$+ \frac{\partial P_{2\underline{det}}(121'2)}{\partial z_1}\Big|_{\substack{1'\to 1\\ r=0}} \hat{k} \qquad (C.37)$$

Using the chain rule and the relationships (B.3) to (B.10)

$$\frac{\partial P_{2\underline{det}}(121'2)}{\partial x_1} = \frac{\partial P_{2\underline{det}}(121'2)}{\partial r_1}\,\frac{x_1}{r_1} \qquad (C.38)$$

$$\frac{\partial P_{2\underline{det}}(121'2)}{\partial x_1}\Big|_{\substack{1'\to 1\\ r=0}} = \frac{\partial P_{2\underline{det}}(121'2)}{\partial r_1}\Big|_{\substack{1'\to 1\\ r=0}}\,\frac{X}{R} \qquad (C.39)$$

and similarly for the other two coordinates. Then,

$$(\nabla_1 P_{2\underline{det}}(121'2)\Big|_{1'\to 1})_{\bar{r}=0} = \frac{\partial P_{2\underline{det}}(121'2)}{\partial r_1}\Big|_{1'\to 1} \frac{X}{R}\hat{i} +$$

$$\frac{\partial P_{2\underline{det}}(121'2)}{\partial r_1}\Big|_{1'\to 1} \frac{Y}{R}\hat{j} + \frac{\partial P_{2\underline{det}}(121'2)}{\partial r_1}\Big|_{1'\to 1} \frac{Z}{R}\hat{k} \qquad (C.40)$$

$$\nabla_1 b(121'2) = \frac{\partial b(121'2)}{\partial x_1}\hat{i} + \frac{\partial b(121'2)}{\partial y_1}\hat{j} + \frac{\partial b(121'2)}{\partial z_1}\hat{k} \qquad (C.41)$$

Using the chain rule and the relationships (C.1) and (C.2) in the equation above

$$\frac{\partial b(121'2)}{\partial x_1} = \frac{1}{2}\frac{\partial b}{\partial R}\frac{X}{R} + \frac{\partial b}{\partial r}\frac{x}{r} \qquad (C.42)$$

and similarly for the other two coordinates. Then,

$$\nabla_1 b(121'2) = \left(\frac{1}{2}\frac{\partial b}{\partial R}\frac{X}{R} + \frac{\partial b}{\partial r}\frac{x}{r}\right)\hat{i} + \left(\frac{1}{2}\frac{\partial b}{\partial R}\frac{Y}{R} + \frac{\partial b}{\partial r}\frac{y}{r}\right)\hat{j}$$

$$\left(\frac{1}{2}\frac{\partial b}{\partial R}\frac{Z}{R} + \frac{\partial b}{\partial r}\frac{z}{r}\right)\hat{k} \qquad (C.43)$$

Therefore,

$$\nabla_1 P_{2\underline{det}}(121'2)\Big|_{\substack{1'\to 1\\ \bar{r}=0}} \cdot \nabla_1 b(121'2)\Big|_{1'\to 1} = \frac{\partial P_{2\underline{det}}(121'2)}{\partial r_1}\Big|_{\substack{1'\to 1\\ \bar{r}=0}} \left(\frac{X^2}{2R^2}\right.$$

$$\left.\frac{\partial b}{\partial R} + \frac{Y^2}{2R^2}\frac{\partial b}{\partial R} + \frac{Z^2}{2R^2}\frac{\partial b}{\partial R} + \frac{X}{R}\frac{\partial b}{\partial r}\frac{x}{r} + \frac{Y}{R}\frac{\partial b}{\partial r}\frac{y}{r} + \frac{Z}{R}\frac{\partial b}{\partial r}\frac{z}{r}\right) \tag{C.44}$$

The equation above, after integration over $\bar{r}$, becomes

$$\int d\bar{r}\ \left(\nabla_1 P_{2\underline{det}}(121'2)\Big|_{\substack{1'\to 1\\ \bar{r}=0}} \cdot \nabla_1 b(121'2)\Big|_{1'\to 1}\right) = \frac{\partial P_{2\underline{det}}(121'2)}{\partial r_1}\Big|_{\substack{1'\to 1\\ \bar{r}=0}}$$

$$\left(4\pi\ \frac{1}{2}\int_0^\infty \frac{\partial b}{\partial R} r^2 dr + \frac{X}{R}\int_0^\infty \frac{\partial b}{\partial r} r^2 dr \int_0^\pi \sin^2\theta\ d\theta \int_0^{2\pi} \cos\varphi\ d\varphi\right.$$

$$+ \frac{Y}{R}\int_0^\infty \frac{\partial b}{\partial r} r^2 dr \int_0^\pi \sin^2\theta\ d\theta \int_0^{2\pi} \sin\varphi\ d\varphi + \frac{Z}{R}\ 2\pi \int_0^\infty \frac{\partial b}{\partial r} r^2$$

$$\left. dr \int_0^\pi \cos\theta \sin\theta\ d\theta\right) \tag{C.45}$$

The second, third and fourth terms in the brackets are zero.

$$\frac{\partial b(121'2)}{\partial R}\Big|_{1'\to 1} = -\frac{\partial(12)}{\partial R} + \varphi(12)\frac{\partial \varphi(12)}{\partial R} \tag{C.46}$$

$$I_3 \equiv \int_0^\infty \frac{\partial \varphi(12)}{\partial R}\ r^2 dr$$

Using equation (C.24) and the integrals (C.4) in the equation above,

$$I_3 = -\frac{d\Phi}{dR}\frac{\sqrt{\pi}}{4\beta^3} - \frac{d\Phi}{dR}\frac{1}{4\beta^3} + \frac{3}{4}\frac{d\beta}{dR}\frac{(\Phi-1)\sqrt{\pi}}{\beta^4} + \frac{\Phi}{\beta^5}\frac{d\beta}{dR} \qquad (C.47)$$

Using equation (C.10) and (C.14),

$$\varphi(12)\frac{\partial\varphi(12)}{\partial R} = (\Phi-1)\frac{d\Phi}{dR}e^{-2\beta^2r^2} - (1-\Phi)\frac{d\Phi}{dR}\,r\,e^{-2\beta^2r^2} - 2\beta\frac{d\beta}{dR}$$

$$(1-\Phi)^2\,r^2\,e^{-2\beta^2r^2} + \beta\frac{d\beta}{dR}\Phi(1-\Phi)\,r^3\,e^{-2\beta^2r^2} + \frac{\Phi}{2}\frac{d\Phi}{dR}\,r\,e^{-2\beta^2r^2}$$

$$+\frac{\Phi}{4}d\Phi\,r^2e^{-2\beta^2r^2} - \Phi\beta\frac{d\beta}{dR}(\Phi-1)\,r^3\,e^{-2\beta^2r^2} - \frac{\Phi^2}{2}\beta\frac{d\beta}{dR}\,r^4\,e \qquad (C.48)$$

$$I_4 \equiv \int_0^\infty \varphi(12)\,\frac{\partial\varphi(12)}{\partial R}\,r^2\,dr$$

with the use of integrals (C.4) and (C.5),

$$I_4 = \frac{(\Phi-1)}{8\beta^3}\frac{d\Phi}{dR}\sqrt{\frac{\pi}{2}} + \frac{(2\Phi-1)}{16\beta^4}\frac{d\Phi}{dR} + \frac{3}{32}\sqrt{\frac{\pi}{2}}\,\frac{1}{\beta^5}\left(\frac{\Phi}{4}\frac{d\Phi}{dR} - 2\beta\frac{d\beta}{dR}\right.$$

$$\left.(1-\Phi)^2 + \frac{\Phi}{4\beta^3}\frac{d\beta}{dR}(1-\Phi) - \frac{\Phi^2}{\beta^4}\frac{d\beta}{dR}\right)\frac{15}{256}\sqrt{\frac{\pi}{2}} \qquad (C.49)$$

$$\left.\frac{\partial P_{2\underline{det}}(121'2)}{\partial r_1}\right|_{\substack{1'\to 1\\ \bar{r}=0}} = \left(\frac{\partial P_1(11')}{\partial r_1}P_1(22) - \frac{1}{2}\frac{\partial P_1(12)}{\partial r_1}\right.$$

$$\left.P_1(21')\right)\Big|_{\substack{1'\to 1\\ \bar{r}=0}} \qquad (C.50)$$

From equations (B.56) and (B.61),

$$\left.\frac{\partial P_1(11')}{\partial r_1}\right|_{\substack{1'\to 1\\ \bar{r}=0}} = \left.\frac{\partial P_1(12)}{\partial r_1}\right|_{\bar{r}=0} = 2 \sum_{ij} P_{ij} \left((n_i-1)\, R^{-1} - \xi_i\right) \psi_i(R)$$

$$\psi_j(R) \qquad \text{(C.51)}$$

and

$$P_1(22)\Big|_{\bar{r}=0} = P_1(21')\Big|_{\substack{1'\to 1\\ \bar{r}=0}} = \rho(R)$$

Then

$$\left.\frac{\partial P_{2\underline{det}}(121'2)}{\partial r_1}\right|_{\substack{1'\to 1\\ \bar{r}=0}} = \rho(R) \sum_{ij} P_{ij} \left((n_i-1)\, R^{-1} - \xi_i\right) \psi_i(R)$$

$$\psi_j(R) \qquad \text{(C.52)}$$

Now Tc_2 is,

$$Tc_2 = 8\pi^2 \int_0^\infty \left(\left.\frac{\partial P_{2\underline{det}}(121'2)}{\partial r_1}\right|_{\substack{1'\to 1\\ \bar{r}=0}} \right) (-I_3 + I_4)\, R^2\, dR \qquad \text{(C.53)}$$

$$Tc_3 \equiv \int d\bar{r}\, d\bar{R}\; \nabla_1^2 P_{2\underline{det}}(121'2)\Big|_{1'\to 1} \qquad b(1212)$$

The quantity $\nabla_1^2 P_{2\underline{det}}(121'2)\Big|_{1'\to 1}$ is expanded in a Taylor series about $\bar{r}=0$ up to zeroth order,

$$Tc_3 = \int d\bar{R} \left(\nabla_1^2 P_{2\underline{det}}(121'2) \Big|_{1' \to 1} \right)_{\bar{r}=0} \int d\bar{r}\; b(1212) \tag{C.54}$$

$$\int d\bar{r}\; b(1212) = 4\pi \int_0^\infty \varphi^2(12)\; r^2\; dr \tag{C.55}$$

because the form chosen for $\Phi(R)$ makes the integral of $\varphi(12)$ over $\bar{r}$ equal to zero.

Using integrals (C.4) and (C.5) in equation (C.55)

$$\int_0^\infty \varphi^2(12)\; r^2\; dr = \frac{(1-\Phi)^2}{8\beta^3}\sqrt{\frac{\pi}{2}} + \frac{\Phi\,(\Phi-1)}{8\beta^4} + \frac{3\,\Phi^3}{128\,\beta^5}\sqrt{\frac{\pi}{2}} = I_5 \tag{C.56}$$

$$\nabla_1^2 P_{2\underline{det}}(121'2) \Big|_{1' \to 1} = \nabla_1^2 P_1(11') \Big|_{1' \to 1} P_1(22) - \frac{1}{2}$$

$$\nabla_1^2 P_1(12) \quad P_1(21)$$

From equations (B.42), (B.56) and (B.64)

$$\nabla_1^2 P_1(11') \Big|_{\substack{1' \to 1 \\ \bar{r}=0}} = \nabla_1^2 P_1(12) \Big|_{\bar{r}=0}$$

and

$$\nabla_1^2 P_1(11') \Big|_{\substack{1' \to 1 \\ \bar{r}=0}} = 2 \sum_{ij} P_{ij}\; (n_i(n_i-1)\; R^{-2} - 2\xi_i n_i)\; \psi_i(R)$$

$$\psi_j(R) \tag{C.57}$$

$$\left(\nabla_1^2 P_{2\underline{det}}(121'2)\Big|_{1'\to 1}\right)_{\bar{r}=0} = \varrho(\bar{R}) \sum_{ij} P_{ij} \left(n_i(n_i-1)\, R^{-2} - 2\right.$$

$$\left.\xi_i n_i\, R^{-1} + \xi_i^2\right)\, \psi_i(R)\, \psi_j(R) \qquad (C.58)$$

And Tc_3 is

$$Tc_3 = 16\pi^2 \int_0^\infty \left(\nabla_1^2 P_{2\underline{det}}(121'2)\Big|_{\substack{1'\to 1 \\ \bar{r}=0}}\right) I_5\, R^2\, dR \qquad (C.59)$$

To evaluate integrals I_1 to I_5 the following derivatives are needed

$$\frac{d\beta(R)}{dR} = \frac{d\,(q\,\varrho^3(R))}{dR} = \frac{1}{3}\, q\, \varrho^{-2/3}(R)\, \frac{d\varrho(R)}{dR} \qquad (C.60)$$

$$\frac{d^2\beta(R)}{dR^2} = \frac{-2}{9}\, q\, \varrho^{-5/3}(R) \left(\frac{d\varrho(R)}{dR}\right)^2 + \frac{1}{3}\, q\, \varrho^{-2/3}(R)\, \frac{d^2\varrho(R)}{dR^2} \qquad (C.61)$$

$$\frac{d\Phi(R)}{dR} = \frac{d}{dR}\left(\frac{\sqrt{\pi}\,\beta(R)}{1+\sqrt{\pi}\,\beta(R)}\right) = \frac{\sqrt{\pi}}{(1+\sqrt{\pi}\,\beta)^2}\left(\frac{d\beta(R)}{dR}\right) \qquad (C.62)$$

$$\frac{d^2\Phi(R)}{dR^2} = \frac{\sqrt{\pi}\,(1+\sqrt{\pi}\,\beta(R))\,(d^2\beta/dR^2) - 2\pi\,(d\beta/dR)^2}{(1+\sqrt{\pi}\,\beta)^3} \qquad (C.63)$$

and from equations (B.56), (B.57), (B.61) and (B.64),

$$\frac{dQ(R)}{dR} = 2 \sum_{ij} P_{ij} \left((n_i + n_j - 2) R^{-1} - (\xi_i + \xi_j) \right) \psi_i(R) \psi_j(R) \qquad \text{(C.64)}$$

$$\frac{d^2Q(R)}{dR^2} = 2 \sum_{ij} P_{ij} \left((n_i + n_j - 2)^2 R^{-2} - (n_i + n_j - 2) R^{-2} - 2 \right.$$
$$\left. (\xi_i + \xi_j)(n_i + n_j - 2) R^{-1} + (\xi_i + \xi_j)^2 \right) \psi_i(R) \psi_j(R) \qquad \text{(C.65)}$$

Equations (C.64) and (C.65) are used to evaluate (C.60) to (C.63), and these to evaluate I_1 to I_5, according to equations (C.29), (C.31), (C.47), (C.49) and (C.56). Thus Tc_1, Tc_2 and Tc_3 are computed, and Tc is obtained as

$$Tc = -1 \, (Tc_1 + 2 \, Tc_2 + Tc_3) \qquad \text{(C.66)}$$

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